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PRINCIPLES AND PRACTICE OF QUALITATIVE ANALYSIS

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PRINCIPLES AND PRACTICE OF QUALITATIVE ANALYSIS

with Semimicro Laboratory Technique

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To

RAYMOND ELLER KIRK

PREFACE

Although the reexamination of the aims of a course is always profitable, it is rarely a simple clear-cut problem. This is especially true of qualitative analysis, which is one of the oldest courses in the chemical curriculum. Although qualitative analysis was originally designed as a course to produce industrial analysts, it has, with the passage of time, changed its objectives many times. At present we teach it to a wide variety of students; some of whom are primarily interested in chemistry, some of whom are interested only in related fields, and few of whom will ever employ it as a tool. In light of these facts, what then should be our aim in teaching qualitative analysis?

We have given much thought to this problem, and this book is, in part, an outgrowth of our ideas. How successful we have been in fulfilling our aims is very difficult for us to judge.

Whereas the first course in chemistry provides the student with a background of facts, theories, and laws, we believe that the second-year course should have two objectives: (1) to present to the student a complete picture of the theory of reactions and (2) to lead him to form an integrated pattern of thought which will effectively guide him in his further studies. Hence in writing the theoretical section of this book, our primary aim has been unity of thought. We have tried to avoid the presentation of the material in "compartmentalized" form even at the risk of disappointing some by omitting their favorite topics. We have tried to show how each topic proceeds logically from the preceding topics and have attempted to teach by precept the art and science of deduction. We believe that qualitative analysis should be made interesting and enjoyable, not by tending toward oversimplification and popularization but, rather, by appealing to the imagination of the student.

With this aim in view, we have presented the mathematical formulations, not as something which the student must memorize, but as a final result to which the student is led through a clear and logical web of thought. On the other hand, we have avoided becoming enmeshed in mathematics, since we believe that subjects which can be very well understood, for elementary purposes, in a qualitative way, should be presented in just such a manner.

On the experimental side, we believe that a student learns, not only by doing, but also by thinking about what he is doing. To further this end we have given very few equations throughout the experimental section. It is our belief that these should be worked out by the student, using the sections on the chemistry of each ion which precedes the preliminary experiments.

Since there is a great tendency on the part of many students to utilize any laboratory text as a "cookbook," we have, as far as possible, designed the experimental directions so as to minimize their ability to do so. Furthermore, we also feel that the methods and apparatus used must be simple even though the semimicro technique is employed. It is also our conviction that the classical qualitative analysis scheme should be taught together with a brief integrated introduction to some of the newer techniques.

Finally, we should always keep in mind this question: What of lasting value will the student retain from the course in qualitative analysis long after he has forgotten most of the details of the analyses?

We wish to acknowledge the help received from many of the standard and more comprehensive works in the field and numerous articles in the original literature. We also wish to acknowledge the encouragement and advice given by Dr. Raymond E. Kirk. Our thanks also go to Dr. Gilbert B. L. Smith for helpful discussions and for the use of some of his mimeographed material on the solubility product; to Dr. H. Mark and Mr. A. L. Davis for assistance in the preparation of the X-ray photograph; to Paul Becher, Irving Myerson, and Mrs. Ruth Weinberger for editorial assistance: to Mrs. Vivian Spoerri, Miss Rose Weinberger, Miss Jane Hammerlund, and Miss Kay Iaconis for the preparation of the manuscript; and to Robert Ryder for assistance in the preparation of the section on solutions. Finally, credit must be given to the many students who aided immeasurably in working out and testing many of the procedures used.

Paul E. Spoerri,
Harold Weinberger,
Robert Ginell.

Brooklyn, N.Y.,
October, 1942.

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CHAPTER I

PRINCIPLES OF ANALYSIS

It is quite natural and commendable that the young student of chemistry should be greatly fascinated by the recent achievements of creative chemistry—the synthesis of vitamins, rubber, dyestuffs, and potent medicinals. However, in his eagerness to make his own contribution, the student is inclined to look upon chemical analysis as an unpleasant and unnecessary delay, a drab course maintained in the curriculum by academic inertia. Hence it seems appropriate to show that such a point of view is not at all justified. In order to build a skyscraper, one must first dig deeply into the ground; this seems like a retreat from the ultimate goal. Similarly, it cannot be disputed that all chemical synthesis rests upon the foundation of chemical analysis.

As an appropriate illustration, let us consider the story of vitamin C. This substance, which prevents the previously dreaded disease called scurvy, is now inexpensive and is available in any quantity. However, the path that led to this end was tortuous. Numerous foodstuffs had to be investigated for the presence of this preventive and curative principle. Proceeding by elimination, as in any chemical analysis, the juices of citrus fruits were found to contain the elusive *X*. In order to isolate the vitamin, the fruit juices had to be taken apart and each component carefully examined. After a long process of selecting, testing, and discarding impotent materials, crystals were finally obtained that had the property of curing scurvy. With this achievement, the vitamin had been isolated in pure form, but before its final synthesis in the laboratory and its ultimate production in a factory, a wide gap, filled with difficulties, had to be bridged. Now the problem was to take apart the pure substance. First the proportions of carbon, hydrogen, and oxygen were determined. Next experiments were performed that differentiated among the various possible combinations of these three elements. These experiments eventually led to a knowledge of the structural formula of the compound; the "blueprint" of the molecule. The stage had now been set for the synthetic chemist. Chemical analysis had drawn up the indis-

pensable blueprint that guided the synthetic chemists' endeavors in building up the molecular structure.

As we have seen, chemical analysis inquires into the composition of substances. It asks two questions: what is present and how much of each substance. For instance, we might wish to know: Does this sample of alluvial sand contain gold? The branch of chemical science that enables us to answer this question experimentally and unequivocally is called qualitative analysis and is the chief concern of this volume. However, this indispensable preliminary which answers the first question (what) must be complemented by an inquiry into the precise quantity of gold present in the sand. The precious metal might be definitely present but in such small quantities that its extraction would be unprofitable. The science that concerns itself with such determinations of quantities is called quantitative analysis.

As in the case of the proverbial housewife, it may justly be said of the analyst that his task never ends. Ever-changing combinations of compounds and newly discovered substances and minerals continually demand the development of new methods, which often tax the ingenuity and skill of the analytical chemist. The astronomer is curious about the rare gases in the atmosphere; the criminologist is concerned with the composition of a certain cigarette ash; the anxious mother wishes to know whether her children's paint set contains any harmful ingredients; and the department-store buyer would like to know whether the silk he contemplates buying is excessively weighted, whether the cotton goods in the last shipment contained inferior dyes or whether the last lot of drugs conformed to government standards.

Although all these problems and many more that confront the chemist demand a wide variety of methods, it is rather reassuring to know that all the methods and principles are based on a single fundamental principle, *the principle of subdivision*. This is really a chemical application of the "divide and conquer" theory so effective in military strategy. Let us assume that a clear, aqueous solution contains about a dozen cations whose identification is desired. It is known that lead, silver, and mercurous ions have one property in common, that of forming relatively insoluble chlorides. If, therefore, we add to this solution chloride ion in the form of dilute hydrochloric acid, the formation of a white precipitate will indicate the presence of at least one of these ions. Naturally, such a precipitate could also indicate that a mixture of two or of all three of the insoluble chlorides was present. In order to obtain further insight into this matter, additional experiments would be required. This precipitate would be labeled "Group I" and reserved for further testing for the presence of the three cations

possibly present. The solution remaining after the separation of this precipitate would now be made slightly acid (by partial neutralization) and saturated with hydrogen sulfide gas. This unpleasant but very useful operation introduces sulfide ion into the solution. Obviously, only those ions having the common property of forming insoluble sulfides under these conditions would precipitate. This property is shared by a number of ions (bismuth, copper, cadmium, arsenic, etc.), and the precipitate, which would be labeled "Group II," must be subjected to further subdivision procedures. This illustration need not be carried further. It is clear that the addition of reagents to the unknown in a definite order would yield groups of precipitates that contain only certain cations. A common qualitative analysis of the cations, recognizes, as a rule, five such groups, as illustrated in the following table:

Group I............	Silver, lead, mercurous mercury
Group II...........	Mercuric mercury, lead, bismuth, copper, cadmium, arsenic, antimony, tin
Group III..........	Nickel, cobalt, manganese, zinc, iron, aluminum, chromium
Group IV..........	Barium, calcium, strontium
Group V...........	Ammonium, sodium, potassium, magnesium

The analyst, having separated all the cations into five groups, is, of course, still far from the completion of his task. He might be compared to the postal clerk who has just completed filing all the incoming letters according to the states to which they are addressed. This is a necessary prerequisite to further division of each pile according to counties, towns, and, finally, streets and numbers. Similarly, the mixture of precipitates representing a group has to be separated into subgroups and finally into compounds containing the individual metals.

The methods for the final and complete identification of ions should also be briefly considered. Lead, which is a constituent of Groups I and II, is selected as an example. The presence of this cation is indicated whenever the addition of hydrochloric acid produces a white precipitate that is soluble in hot water. Scientific thoroughness, however, demands further evidence.

A reference book or the original literature may be consulted, wherein will be found a wide variety of experiments concerning the characteristic reactions of the lead ion. Obviously, it would not be expedient to do all these experiments, and a choice must be made. In this selection, we are guided by considering carefully the **specificity** and **sensitivity** of a test reagent. A reagent would be called specific for lead ion if it gave a definite reaction (precipitate, colored solution, etc.) in the presence of

lead only but no similar reaction in the absence of lead ion, regardless of the presence of any other ion. Such reagents, serving only one master, are unknown. Their allegiance is usually divided. Dimethyl glyoxime, a reagent for nickel ion, comes closest to being the ideal specific reagent. It gives a very characteristic red precipitate with nickel in the presence of any or all Group III cations; halogens, however, interfere with this test. Therefore, the possibility of interfering ions should be carefully considered and reagents chosen that are not affected by these possible interferences. Benzidine reagent, for instance, gives a positive color reaction with chromate ion, with manganese dioxide, and with lead dioxide. However, the use of benzidine for the identification of lead ion in Group I is justified, since both chromates and manganese dioxide are obviously absent.

In order to understand the sensitivity of a test, the following simple experiments may be considered. Starting with a lead ion stock solution of known concentration, a series of more and more dilute solutions of known concentration are prepared. One milliliter of each solution is placed in a test tube and the tubes arranged in the order of decreasing concentration (the first tube, for example, containing 10 mg. of lead ion, the second only 5 mg., etc.). An equal quantity of reagent (*e.g.*, 2 drops), such as potassium chromate, K_2CrO_4, is added to each solution. This experiment would show clearly how the concentration of the ion would influence the test. In the first tubes, the precipitate would be relatively copious, and the identification, therefore, would be quite decisive. The volume of precipitate would steadily decrease until we reached a test tube where the precipitate would be barely visible. This last test would be positive, but a further decrease of the lead ion concentration would lead to an uncertain test. The concentration of this solution would be noted and designated as the **limit of detection** of lead ion with potassium chromate or chromate ion. Such concentrations are conventionally expressed in thousandths of a milligram, or gamma (γ) per drop (0.02 ml.). Repetition of this type of experiment with other reagents reveals the fact that the limit of detection varies. Let us assume that reagent A has a limit of detection of 10γ of lead ion, whereas reagent B has a limit of detection of $0.1\ \gamma$ of lead ion. Expressed differently, this would mean that B is a far more sensitive reagent than A.

In toxicology, the branch of chemical analysis dealing with poisons, reagents must be selected with special reference to their sensitivity. Indeed, it would be senseless to test for minute amounts of poisons with a reagent of poor sensitivity. This does not mean that we should invariably select reagents of the greatest possible sensitivity. Some

reagents, such as dithizone, are far too sensitive for our laboratory work.

To summarize, in selecting a reagent for a final identification test, preference should be given to reagents possessing (1) fair specificity; the reagent should not give a similar reaction with any possible contaminants of the test solution and (2) fair sensitivity, permitting unequivocal detection.

CHAPTER II

THE PERIODIC AND ANALYTICAL CLASSIFICATION OF THE ELEMENTS

The successful practice of analytical chemistry seems at first quite arduous, since it appears to demand the memorization of a multitude of unrelated and unpredictable facts, such as the solubility of aluminum hydroxide in acids and bases or the solubility of arsenous sulfide in ammonium polysulfide, etc. Although a certain amount of memorization is indispensable, the task is considerably lightened by a knowledge of the periodic arrangement of the elements. This system arranges the elements so that it is possible to predict the properties of one element from a knowledge of the properties of another. For instance, knowing that phosphorus has the valences 3 and 5 and that phosphorus trioxide and phosphorus pentoxide each form three acids, we can predict that arsenic, which is in the same family of elements, will form similar compounds that will have analogous properties.

The periodic classification of the elements was formulated by Mendelejeff in 1869. This achievement was the culmination of a series of attempts by early nineteenth century chemists to arrange the elements on the basis of similarities in their chemical properties. Mendelejeff's original table of the elements has since been modified and extended. More recently, the periodic arrangement has been shown to depend on a more fundamental quantity than the atomic weight, namely, the atomic number.

The Periodic Table.—In his original classification, Mendelejeff arranged the elements in the order of their increasing atomic weights. He found, in so doing, that the properties of the seven elements from lithium to fluorine varied systematically in progressing from the first to the last named element. The next element, sodium, resembled lithium in its properties and reactions, and from this point, the variation in properties progressed again, through the same number of elements, to chlorine, *i.e.*, each element in this second progression resembled a corresponding element in the first series. Upon continuing this scheme, Mendelejeff found that all the elements could be arranged in a series of horizontal and vertical groups, in which the adjoining elements exhibited a gradation of properties. In certain cases, it was

found that the atomic weights of several elements (the factor determining their positions) were at variance with the known chemical properties. Since the general chemical properties of these elements were known with certainty, there were, therefore, two alternatives. Either the atomic weights, as then known, were incorrect, or the whole concept of periodicity was invalid. Boldly, Mendelejeff relied on the chemical properties in placing these elements and predicted that the atomic weights were incorrect. At other points where no known elements could be placed, he left blank spaces and also predicted the general properties of the undiscovered elements that would fit into the table properly. Most of these were subsequently discovered and isolated. One form of representation of the periodic table is given in Table I.

TABLE I.—THE PERIODIC CLASSIFICATION OF THE ELEMENTS

Series	Group															
	1a	2a	3a	4a	5a	6a	7a	8	1b	2b	3b	4b	5b	6b	7b	0
I	H 1															He 2
II	Li 3	Be 4									B 5	C 6	N 7	O 8	F 9	Ne 10
III	Na 11	Mg 12									Al 13	Si 14	P 15	S 16	Cl 17	A 18
IV	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe Co Ni 26 27 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
V	Rb 37	Sr 38	Y 39	Zr 40	Cb 41	Mo 42	Ma 43	Ru Rh Pd 44 45 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
VI	Cs 55	Ba 56	La* 57	Hf 72	Ta 73	W 74	Re 75	Os Ir Pt 76 77 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	— 85	Rn 86
VII	— 87	Ra 88	Ac 89	Th 90	Pa 91	U 92										

* Elements 57 to 71 are rare-earth elements:

La	Lanthanum	57	Gd	Gadolinium	64
Ce	Cerium	58	Tb	Terbium	65
Pr	Praseodymium	59	Dy	Dysprosium	66
Nd	Neodymium	60	Ho	Holmium	67
Il	Illinium	61	Er	Erbium	68
Sm	Samarium	62	Tm	Thulium	69
Eu	Europium	63	Yb	Ytterbium	70
			Lu	Lutecium	71

Atomic Numbers.—Following the publication of Mendelejeff's periodic table, numerous investigations were undertaken to prove or disprove his contentions regarding the incorrectness of certain atomic weights. In most of these anomalies, the periodic table was shown to be correct, and these atomic weights were subsequently revised.

TABLE II.—ELECTRON DISTRIBUTION IN THE ELEMENTS

Element	Atomic number	K	L		M			N				O					P						Q
			2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1
H	1	1																					
He	2	2																					
Li	3	2	1	0																			
Be	4		2	0																			
B	5	K	2	1																			
C	6	shell	2	2																			
N	7	com-	2	3																			
O	8	plete	2	4																			
F	9		2	5																			
Ne	10		2	6																			
Na	11	2	2	6	1	0																	
Mg	12				2	0																	
Al	13	K and L			2	1																	
Si	14	shells			2	2																	
P	15	complete			2	3																	
S	16				2	4																	
Cl	17				2	5																	
A	18				2	6																	
K	19	2	2	6	2	6	0	1															
Ca	20						0	2															
Sc	21						1	2															
Ti	22	K and L					2	2															
V	23	shells					3	2															
Cr	24	complete					5	1															
Mn	25						5	2															
Fe	26						6	2															
Co	27						7	2															
Ni	28						8	2															
Cu	29						10	1															
Zn	30							2															
Ga	31				M shell			2	1														
Ge	32				complete			2	2														
As	33							2	3														
Se	34							2	4														
Br	35							2	5														
Kr	36							2	6														
Rb	37	2	2	6	2	6	10	2	6	0		1											
Sr	38									0		2											
Y	39									1		2											
Zr	40									2		2											
Cb	41		K, L, and M							4		1											
Mo	42		shells							5		1											
Ma	43		complete							6		1											
Ru	44									7		1											
Rh	45									8		1											
Pd	46									10		0											
Ag	47											1											
Cd	48											2											
In	49											2	1										
Sn	50											2	2										
Sb	51											2	3										
Te	52											2	4										
I	53											2	5										
Xe	54											2	6										

TABLE II.—ELECTRON DISTRIBUTION IN THE ELEMENTS.—(*Continued*)

Element	Atomic number	*K*	*L*		*M*			*N*				*O*					*P*						*Q*
			2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1
Cs	55	2	2	6	2	6	10	2	6	10		2	6	0			1						
Ba	56													0			2						
La	57	*K*, *L*, and *M* shells complete												1			2						
Ce	58	2	2	6	2	6	10	2	6	10	1	2	6	1			2						
Pr	59										2			1			2						
Nd	60										3			1			2						
Il	61										4			1			2						
Sm	62		*K*, *L*, and *M* shells								5			1			2						
Eu	63		complete								6			1			2						
Gd	64										7			1			2						
Tb	65										8			1			2						
Dy	66										9			1			2						
Ho	67										10			1			2						
Er	68										11			1			2						
Tm	69										12			1			2						
Yb	70										13			1			2						
Lu	71										14			1			2						
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2			2						
Ta	73													3			2						
W	74	*K*, *L*, *M*, and *N* shells complete												4			2						
Re	75													5			2						
Os	76													6			2						
Ir	77													7			2						
Pt	78													9			1						
Au	79	2	2	6	2	6	10	2	6	10	14	2	6	10			1						
Hg	80																2						
Tl	81																2	1					
Pb	82	*K*, *L*, *M*, *N*, and *O* shells complete except 5_4 and 5_5															2	2					
Bi	83																2	3					
Po	84																2	4					
—	85																2	5					
Rn	86																2	6					
—	87	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6					1
Ra	88																						2
Ac	89																		1				2
Th	90	*K*, *L*, *M*, *N*, and *O* shells complete except 5_4 and 5_5																	3				1
Pa	91																		4				1
U	92																		5				1

There were, however, several pairs of elements whose properties demanded one arrangement but whose atomic weights, accurately rechecked, demanded another. These anomalies proved to be a stumbling block for many years and were not cleared up until the work of the English physicist Moseley in 1913–1914. Using the methods of X-ray spectroscopy, he found that there existed a property of the elements more fundamental than atomic weights. This property is called the atomic number. It represents the number of

positive charges in the nucleus of the atom or, conversely, the total number of electrons about the nucleus. In this manner, all the elements from hydrogen through uranium may be assigned numbers from 1 to 92.

Electron Shells.—It may be seen from the foregoing that the chemical behavior of the elements will depend upon their atomic number (*i.e.*, number of electrons) and upon some periodic variation due to the arrangement of the electrons about the nucleus. The modern atomic theory postulates that the nucleus of the atom is surrounded by a series of concentric shells containing electrons. **It should be clearly understood that these are not actual solid shells but are, rather, a symbolic representation.** The first shell, called the *K* shell, contains two electrons when filled. The second shell, the *L* shell, contains eight electrons when completed, etc. The number of electrons in the outermost shell determines the chemical properties of the element. Table II shows the electron distribution in shells for each element.

Vertical Relationships.—The construction of the periodic table (Table I) is such that the elements in the vertical groups or families bear a strong chemical resemblance to each other. For example, the members of Group 1*a* (lithium, Li, sodium, Na, potassium, K, rubidium, Rb, and cesium, Cs) exhibit a usual valence of positive 1. Their hydroxides, which have the general formula MOH, are all strong bases and are quite soluble in water. The strongest base is cesium hydroxide, and the weakest is lithium hydroxide. The general formula of the hydroxides of the elements of Group 2*a* (calcium, Ca, barium, Ba, and strontium, Sr) is $M(OH)_2$. These are also strong bases but have only a limited solubility in water.

The base-forming character of the elements decreases through the next several groups through the amphoteric, or transitional, elements to the acid-forming elements. In Group 7*b*, for example, are the elements fluorine, chlorine, bromine, and iodine, the so-called halogens. The compounds of the halogens with hydrogen are fairly strong acids in aqueous solution, decreasing in stability to HI. These elements, with the exception of fluorine, also form oxygen acids, which are active oxidizing agents.

The remaining vertical groups exhibit similarities of the same type. The elements of Group 6*b*—sulphur, S, selenium, Se, and tellurium, Te—all form similar hydrogen compounds having the general formula H_2X. These are all gases with foul odors and are slightly soluble in water with the formation of weak acids. They function as precipitants with many metallic ions and are also good reducing agents. They form a series of strong oxygen acids and give rise to oxides of formula

XO_2 and XO_3. The last member of the group, polonium, Po, is one of the radioactive elements and is quite rare. Its reactions have not been fully investigated, but it probably reacts in the same fashion as the other members of the group. Similarly, the reactions of phosphorus, arsenic, antimony, and bismuth follow the same general family relationships. It should be remembered that there is a gradation of properties from the first element in a vertical group to the last, and therefore the first may bear only a superficial relationship to the last element. However, the elements in the middle of a group will resemble each other more closely.

One more important point must be considered in this section. Hydrogen, in Group 1, appears to fall in two families. First, in some of its reactions, it resembles the alkali metals of Group 1*a* and forms stable compounds with the elements of Group 7*b*, having the formula HX, and with the elements of Group 6*b*, where the formula is H_2X. In these reactions, hydrogen has a valence number of positive 1. Similarly, it also appears to belong to Group 7*b*, since it forms hydrides with the alkali metals of formula MH and with Group 2 metals, where the formula is MH_2. Here hydrogen has a valence number of negative 1.

In general, the first member of each vertical group exhibits some anomalous reactions. This is generally attributed to the smaller atomic volume of the element. The boiling point of the hydrogen halides of Group 7*b*, varies thus:

$$\mathrm{HI} = -36°\mathrm{C.},\ \mathrm{HBr} = -68°\mathrm{C.},\ \mathrm{HCl} = -83°\mathrm{C.},\ \mathrm{HF} = +19.4°\mathrm{C.}$$

It can be seen that the boiling point of hydrogen fluoride is anomalous. This is attributed to the small volume and extreme reactivity of fluorine. HF reacts with another HF to form the dimer H_2F_2. Other examples of the anomalous behavior of the first members are oxygen in Group 6*b* and nitrogen in Group 5*b*, both of which are gases, whereas the other members of both groups are solids.

Horizontal Relationships.—In addition to the strong chemical resemblances noted among the members of the vertical groups or families of elements, there exist, also, marked similarities among a number of elements in the various horizontal series in the periodic table. In the first three series, those beginning with hydrogen, lithium, and sodium, respectively, the adjoining elements exhibit little similarity in properties but demonstrate, rather, a marked difference in progressing from one to the other. However, in the fourth series, that which begins with potassium, the first few elements, notably potassium and calcium, exhibit the same marked difference, but this

gradation in properties ends with a series of elements that show many similarities in properties. This series continues to Group 8 (iron, cobalt, and nickel), where the similarities among the members of this group are so pronounced that they are placed together in one group and considered as a single element in the periodic arrangement. These elements are commonly known as transitional elements. From this point, the elements return to the point where marked gradations in properties are again noted.

In the first two (short) series, the elements gradually decrease in metallic character in progressing from Group 1*a* across to Group 7*b*. However, the "trough" elements in the first long series are all metals. The same may be said regarding the second long series. In the third long series (Series VI), the trough character is greatly extended, and from element 57 (lanthanum) to element 72 (hafnium), there are 14 elements whose properties are remarkably similar (the rare-earth metals). In fact, they are so closely related that they are usually found associated in their ores and complex minerals and are exceedingly difficult to separate. They have all been isolated, in the form of their salts, by laborious and elaborate fractional-crystallization procedures.

This same close relationship is also shown among the elements of Group 8, where nickel is more frequently found associated with cobalt in ores than with palladium and where platinum is more frequently found with osmium and iridium than with palladium (see Table I). The student should note carefully that, although the vertical relationships of the elements are important, in many cases, particularly among the trough elements of the long series, the horizontal relationships are just as important and sometimes are even more important.

Diagonal Relationships.—A third type of relationship among the elements, in addition to the two types discussed above, is worthy of mention. This is the diagonal relationship that the elements bear to each other in the periodic classification. It appears that certain elements usually have some chemical resemblance to the elements diagonally below them to the right. This is especially true of the elements of the first series. Beryllium, although it has a valence number of positive 2 and forms a chloride $BeCl_2$, strongly resembles aluminum, which has a valence of positive 3 and forms a chloride $AlCl_3$, rather than magnesium, which is just below it in Group 2*a*. In fact, beryllium is rather difficult to separate from aluminum. Another example is that of lithium, which resembles magnesium in its reactions. Similarly, boron is a nonmetal like silicon, its diagonal partner, rather than a metal like aluminum, which is in the same

family. Other resemblances of the same sort are to be found throughout the periodic table, although these are not so pronounced as the examples cited.

ANALYTICAL GROUPING OF THE ELEMENTS

Twenty-one elements are generally included in the conventional schemes of qualitative analysis. In addition, two different valence forms of mercury (mercurous and mercuric ions) are considered individually, and lead, by virtue of the slight solubility of its chloride, is considered in two separate groups. The ammonium ion, which resembles the alkali metals closely in its chemical properties, is also included, making a total of 25 cations (Table III). For analytical

TABLE III.—ELEMENTS INCLUDED IN THE USUAL SCHEMES OF CATION ANALYSIS

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

purposes, these metals are divided into five groups, based upon their reactions with various reagents. This method is based primarily upon the solubilities of various compounds of the ions and is, therefore, an arbitrary arrangement. Obviously, other methods of grouping could, and have been, worked out, but the arrangement given in this text is, with some variations, the most convenient and that which is almost universally used. It should be noted, too, that this arrangement is not based entirely upon the periodic system, but a study of the various figures will show that a close similarity does exist among the vertical, horizontal, and diagonal relationships in the periodic table and the analytical grouping of the metals.

The Groups.—The elements are divided as follows:

Group I contains those metals which form insoluble or sparingly soluble chlorides. These are silver, lead, and mercurous mercury. The group reagent is Cl^-, usually in the form of dilute hydrochloric acid. Since lead chloride is slightly soluble in water, sufficient lead ion remains in solution to make it necessary to test for the cation again in Group II. Table IV shows the elements that form insoluble chlorides and their relationships in the periodic table.

Group II consists of those metallic ions which yield sulfides that are insoluble in dilute acids. These are usually precipitated, after the removal of Group I, by the use of hydrogen sulfide gas in solutions about 0.25 to 0.5N with respect to hydrochloric acid. The elements thus precipitated are: mercuric mercury, Hg, lead, Pb, bismuth, Bi, copper, Cu, cadmium, Cd, arsenic, As, antimony, Sb, and tin, Sn. The group is further subdivided into subgroups A and B by the solvent action of ammonium polysulfide on the sulfides of the three last elements (Tables V, VI, VII).

Group III comprises those cations that yield sulfides that are soluble in dilute acids but that are insoluble in neutral or alkaline medium and those ions that form insoluble hydroxides with ammonia. This group, therefore, is precipitated by hydrogen sulfide from ammoniacal solution (ammonium sulfide). The relation of these elements in the periodic table is illustrated in Tables VIII, IX, X.

Group IV metals are those which form soluble sulfides under the conditions given above but which yield other insoluble salts after the separation of the previous groups. The alkaline earth elements (calcium, barium, and strontium) comprise this group, as shown in Table XI.

Group V contains those elements not precipitated by any of the reagents previously used. These are magnesium, the alkali metals, sodium and potassium, and ammonium ion. These are generally identified individually in the final filtrate, although the test for ammonium ion is usually performed at the beginning of an analysis (Table XII).

Use of the Analytical Tables.—In attempting to predict the chemical properties of any element, it should always be borne in mind that there are three types of similarities (vertical, horizontal, and diagonal relationships) which must be weighed and balanced before a decision is made. In Tables IV to XII, it has been shown how the elements react to certain specific and commonly used reagents. For example, if a chemist should have occasion to analyze a sample suspected of containing germanium, what could he say about the likely properties

TABLE IV.—GROUP I METALS

ELEMENTS THAT FORM INSOLUBLE OR SPARINGLY SOLUBLE CHLORIDES

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

Light block indicates element that is not considered in the usual schemes of cation analysis.

TABLE V.—GROUP II METALS

ELEMENTS THAT FORM INSOLUBLE SULFIDES IN 0.25 TO 0.5N ACID SOLUTIONS

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As		Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd		Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

Light blocks indicate elements that are not considered in the usual schemes of cation analysis. Circles indicate elements previously removed.

TABLE VI.—GROUP II*A* ELEMENTS

ELEMENTS THAT YIELD SULFIDES INSOLUBLE IN AMMONIUM POLYSULFIDE

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag		In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

Light blocks indicate elements that are not considered in the usual schemes of cation analysis. Circles indicate elements previously removed.

TABLE VII.—GROUP II*B* ELEMENTS

ELEMENTS THAT YIELD SULFIDES SOLUBLE IN AMMONIUM POLYSULFIDE

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	
—	Ra	Ac	Th	Pa	U												

Light blocks indicate elements that are not considered in the usual schemes of cation analysis.

TABLE VIII.—GROUP III ELEMENTS

ELEMENTS THAT YIELD INSOLUBLE SULFIDES OR HYDROXIDES WITH AMMONIUM SULFIDE AND AMMONIUM HYDROXIDE

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

Light blocks indicate elements that are not considered in the usual schemes of cation analysis. Circles indicate elements previously removed.

* Including rare-earth elements.

TABLE IX.—GROUP IIIA ELEMENTS

ELEMENTS THAT FORM INSOLUBLE HYDROXIDES WITH AMMONIUM SULFIDE AND AMMONIUM HYDROXIDES

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

Light blocks indicate elements that are not considered in the usual schemes of cation analysis. Elements previously removed are not included in this figure.

* Including rare earths.

TABLE X.—GROUP III*B* ELEMENTS

ELEMENTS THAT FORM INSOLUBLE SULFIDES WITH AMMONIUM SULFIDE AND AMMONIUM HYDROXIDE

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

Light blocks indicate elements that are not considered in the usual schemes of cation analysis. Elements previously removed are not included in this figure.

TABLE XI.—GROUP IV ELEMENTS

ELEMENTS PRECIPITATED BY AMMONIUM CARBONATE AND AMMONIUM CHLORIDE

(After the separation of the previous groups; other methods also used)

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

Light block indicates elements that are not considered in the usual schemes of cation analysis.

TABLE XII.—GROUP V ELEMENTS
ELEMENTS THAT FORM SOLUBLE COMPOUNDS WITH THE REAGENTS USED PREVIOUSLY

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

Light blocks indicate elements that are not considered in the usual cation-analysis schemes.

TABLE XIII.—ELEMENTS NOT INCLUDED IN THE PREVIOUS TABLES

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

Light block indicates rare gases—chemically inert (as usually understood).
Heavy block indicates elements usually encountered as anions.
Dotted block—little is known of chemistry, although probably similar to Se and Te.
Circle—very active chemically—special analytical methods employed. Always present in aqueous systems.

of this element and its compounds before consulting a reference book? Looking at Table I, he would find that it is in Group 4*b*, situated between silicon and tin. Silicon is a nonmetal, and tin is a metal; germanium should then be somewhere in between. In the horizontal series in which it occurs, it lies between zinc, an amphoteric metal, and arsenic, which is less metallic and also amphoteric; therefore he could safely predict that germanium will be amphoteric. From Table VI, we see that it falls into the analytical Group II*B*. We could also, from a knowledge of the chemistry of its surrounding elements, say that it should hydrolyze in water forming an oxy compound. We have now deduced some pertinent information about this element, and we can proceed with the analysis of the other groups but expect to have difficulties in group II*B*. With the knowledge at hand, a reference book should now be consulted for the exact modifications to be introduced in the group II*B* analysis.

READING REFERENCES

Hildebrand, J. H.: "Principles of Chemistry," 4th ed., Chap. XVII, The Macmillan Company, New York, 1940.

Meldrum, W. B., and F. T. Gucker: "Introduction to Theoretical Chemistry," Chap. I, American Book Company, New York, 1936.

Moore, F. J.: "A History of Chemistry," 2d ed., Chap. XVI, McGraw-Hill Book Company, Inc., New York, 1931.

Quam, M. B., and G. N. Quam: Types of Graphic Classification of the Elements, *J. Chem. Educ.*, Vol. 11, January, April, and May, 1934.

Weeks, M. E.: "The Discovery of the Elements," Chap. XIV and XV, Mack Printing Company, Easton, Pa., 1935.

QUESTIONS

1. Using a periodic chart of the elements, predict the formulas of the following compounds of the element whose atomic number is 38: Oxide, chloride, sulfate, nitrite.

2. Using a periodic chart of the elements, predict the formula of the following compounds of the element whose atomic number is 81: Oxides, chloride, nitrate, phosphate.

3. With what element or elements would you expect cadmium to be associated in ores?

4. How many electrons are there in the outermost shell of the following elements: vanadium, rhenium, beryllium, aluminum, radium.

5. Given that the density of sulfur is 2.07 and that the density of tellurium is 6.24, what would you predict that the density of selenium would be? Compare this value with that given in the literature, and calculate your percentage error.

6. Given that the melting point of potassium is 62.3°C. and that the melting point of cesium is 28.5°C., what would you predict that the melting point of rubidium would be? Compare this value with that given in the literature, and calculate your percentage error.

7. If you suspected that you had columbium in an unknown, in what analytical cation group would you look for it?

8. In what analytical group would gold precipitate if it were present in one of your unknowns?

9. An analyst who specializes in the analysis of the noble metals is concerned chiefly with what analytical groups?

10. What arrangement of the electrons characterizes a rare gas?

CHAPTER III

THE ATOM AND THE MOLECULE

Although no one, to date, has seen an individual atom, scientists have nevertheless been able to gather a multitude of data and information about them and, as a consequence, have tried to imagine what atoms look like. In the earlier pictures, the atom consisted of a small positively charged nucleus, around which rotated negatively charged electrons in some sort of orbits.

However, this picture was not quite satisfactory, since it was found that an atom constructed on this plan would not behave as a real atom does. For instance, a real atomic system emits light of a *definite* wave length (energy) when heated. In the simple model mentioned, the rotating electron would continuously emit energy of changing wave length and would revolve in a spiral that became smaller and smaller until the electron struck the nucleus.

The frequency (the number of waves per second) is related to the wave length (the length of each wave) by velocity, since number (of waves) times centimeters gives centimeters per second, which has the dimensions of velocity. This can be represented by the formula

$$\nu\lambda = v$$

where v = velocity
ν = frequency
λ = wave length

The Hydrogen Atom.—Niels Bohr formulated an empirical solution to this problem. His model is similar to this simple one except that the electrons are permitted to travel only in orbits of certain fixed diameters and not in all possible orbits (and therefore can never fall into the nucleus). He arrived at this concept quite empirically, *i.e.*, he found that if he imposed this condition, called the quantum condition, on a model built on classical lines, the model would behave like a real atom. In the picture that he proposed, an electron revolving about the nucleus would not emit energy (as light) but on jumping from one orbit to another orbit, would emit light. The frequency of this light could be calculated simply. The energy that the electron possessed at each level could be calculated from classical mechanics, and the difference between the energies at these two levels would

represent the energy emitted as light of a definite frequency. The relationship between the energy and frequency is simple. The energy equals the frequency times h (Planck's constant) or

$$E = h\nu$$

where E = energy
ν = frequency
h = Planck's constant

It was now possible to draw a schematic picture of the hydrogen atom according to this theory. In going from a higher energy level to a lower energy level, the electron emits light or energy; in going from a lower energy level to a higher one, it absorbs energy or light. When a vapor is heated, the electrons jump to higher levels and absorb energy, and in falling back to lower levels, they emit light, which, when

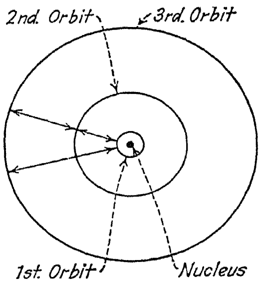


FIG. 1.—Schematic picture of some possible circular orbits (energy levels) of the electron in the hydrogen atom.

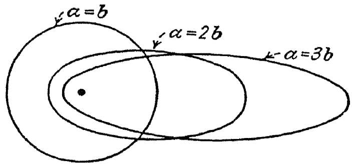


FIG. 2.—Schematic picture of some circular and elliptical orbits of the electron in the hydrogen atom.

analyzed spectroscopically, appears as a series of lines (of fixed position for each element) of characteristic wave length.

Later it was realized that when one body revolves around another body, it does not usually move in a circular path but, rather, in an elliptical one. This is known from a study of both theoretical mechanics and practical astronomy. It has long been known that the orbits of the planets around the sun are elliptical rather than circular, with the sun at one of the focuses. This refinement of the Bohr theory resulted in a change in the concept of the atom. The orbits were now elliptical, as shown in Fig. 2.

This newer concept explained fairly adequately the structure of the hydrogen atom, but it was not so successful when more complicated atoms were considered. Furthermore, it was not clearly understood why this quantum condition was necessary.

An explanation of this problem was soon forthcoming. De Broglie and Schroedinger changed the concept of the atom by inventing a new tool, quantum mechanics, and endowed the empirical relationship of Bohr with a theoretical explanation. By the use of higher mathe-

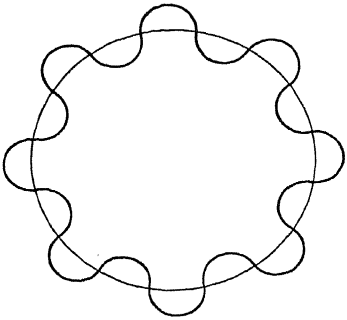


FIG. 3.—Circular standing wave: permissible orbit.

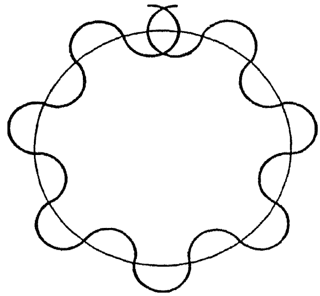


FIG. 4.—Circular wave interferes with itself: nonpermissible orbit.

matics (beyond the scope of this book), they derived a basis for Bohr's quantum condition. On a simplified basis, the reason for this condition can be made intelligible. Let us first consider that the electron, in addition to being a particle, is also a wave traveling in a circular orbit around a nucleus, as in Fig. 3. This wave is continuous, a sort of a stationary wave. If, however, the circumference of the orbit is slightly decreased, stationary waves cannot be produced, but each wave will interfere with the preceding wave (as in Fig. 4) and produce beats and interference. Therefore, it is evident that stationary waves of a certain wave length will exist only in certain orbits of fixed radii. This is a very simplified two-dimensional picture of Schroedinger's explanation of Bohr's quantum condition. De Broglie's and Schroedinger's theories, therefore, changed the hitherto material particle, the electron, into an electrical-charge density or a wave in an electrical cloud. This latter statement may seem almost unintelligible, but it has meaning.

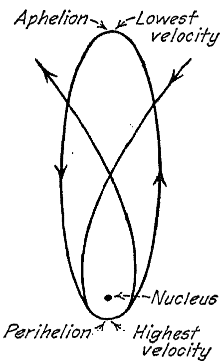


FIG. 5.—Path of electron traveling in an elliptical orbit around the nucleus.

M. Born has given a new interpretation to this concept. According to him, "the electrical charge density in an electrical cloud," considered statistically is nothing more than the probability of finding a

material particle, an electron, in any position around a nucleus. One way of interpreting this statement is as follows. Let us look at an electron traveling in an elliptical orbit around a nucleus. The speed of the electron will not be constant because, according to Kepler's laws of motion, the area swept by a body moving around another one is the same for each period of time. Therefore, the electron will move most rapidly when it is nearest the nucleus (at the perihelion) and least rapidly when it is farthest from the nucleus (at the aphelion). According to Einstein's theory of relativity, the more rapidly a body moves the greater its mass. This effect, although only very slight at ordinary velocities, is enhanced as the body approaches the velocity of light.

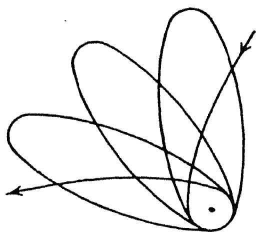


FIG. 6.—Precession of the elliptical orbit of the electron.

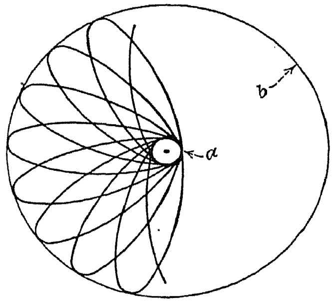


FIG. 7.—Limits of a precessing orbit.

Therefore, since the electron moves with a very high velocity, any change in this velocity will give rise to a pronounced effect on the mass. The electron, therefore, has a greater mass because of its greater velocity when it is nearer the nucleus. The curvature of the orbit depends upon the mass and velocity of the electron, and, as a consequence, the path the electron returns upon will not be the mirror image of the path it originally traversed, and the elliptical orbit will precess (see Fig. 6).

The electron will therefore never approach closer to the nucleus than circle a (Fig. 7) or go farther than circle b, and we may consider the space between a and b as being an electrical cloud of variable electrical density, or we may consider the statistical probability of finding the electron in any small area between a and b. As is evident from the drawing, the probability of finding an electron in a small area near the nucleus is greater than finding it far away from the nucleus.

Another method of describing the atom is by means of Heisenberg's matrix mechanics. Unfortunately, no one has yet been able to

derive a model or picture of the atom from his mathematical equations, which are quite complicated and which will, as a consequence, not be considered.

We see, therefore, that an electron is a many-sided object that assumes varied aspects, depending upon one's vantage point. The objective, then, determines which aspect of the electron is used.

The structure of the nucleus, the other half of the hydrogen atom, (if it has a structure?) is a complete mystery to science. All that can be said about the hydrogen nucleus, or proton, is that it is singly positive in charge, has a mass of about 1.65×10^{-24} gram and a radius of the order of 10^{-13} cm.

Thus far, the physical aspects of the structure of the hydrogen atom have been considered. Since our subject of study is elementary chemistry, we shall consider henceforth the atom in two relatively simple ways, which will serve to explain most of the phenomena that we shall encounter. In the first picture, the nucleus is represented by a dot and the electrons by other dots around it, as in Fig. 8.

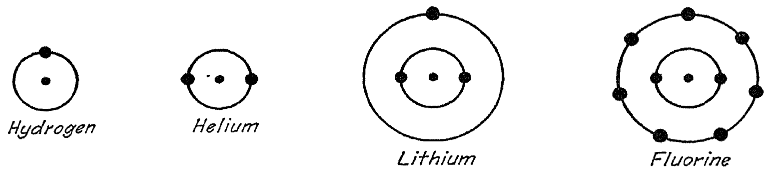


FIG. 8.—Symbolic representation of electronic structure.

In the second picture, the nucleus and all the electrons in the inner shells are represented by the symbol of the element, and the electrons in the outermost shell are represented by dots. If any electrons were originally present and were later removed because of reactions, no dots are indicated (see lithium atom and lithium ion). The magnitude of the charge on the atom is indicated by the appropriate symbols (+ or −).

$\mathrm{H}\cdot$		$\cdot\mathrm{He}\cdot$	$\mathrm{Li}\cdot$		$\mathrm{Na}\cdot$	Na^+
Hydrogen atom	Hydrogen ion	Helium atom	Lithium atom	Lithium ion	Sodium atom	Sodium ion
$:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot$	$:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:^-$	$\mathrm{Cu}:$	Cu^{++}			
Chlorine atom	Chloride ion	Copper atom	Cupric ion			

The student should always remember that these are only symbols and not actual pictures of atoms.

Other Atoms.—As was pointed out in Chap. II, the elements exhibit a periodic gradation in properties. This can be explained on

an electronic basis. Hydrogen, with an atomic number of 1, has one electron revolving around the nucleus, and it may be represented as in

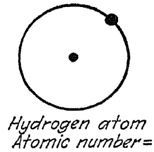


FIG. 9.

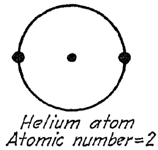


FIG. 10.

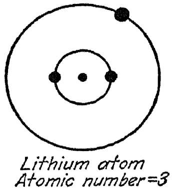


FIG. 11.

Fig. 9. Helium, with an atomic number of 2, has two electrons revolving around it, as in Fig. 10. The next element is lithium, which has an atomic number of 3. It could be written as in Fig. 12, but it is known that lithium is somewhat similar to hydrogen in its reactions, and Fig. 9 does not resemble Fig. 12 in the slightest. If, however, we now write lithium as in Fig. 11, it would bear some resemblance to Fig. 9; both representations have a lone electron in their outer ring. The following elements to neon, atomic number 10, would then appear as in Fig. 13.

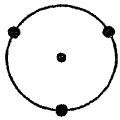


FIG. 12.

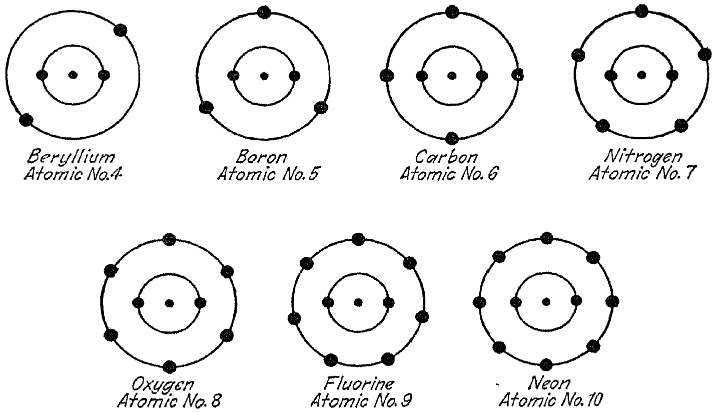


FIG. 13.—Symbolic representation of the remaining members of the second series.

Neon, atomic number 10, is an inert gas and resembles helium; the next element sodium, atomic number 11, resembles lithium in its reactions and should evidently have a lone electron in its outer ring and could be represented as in Fig. 14. The same idea may be applied in the formulation of the pictures of all the other elements. However, since this symbolism becomes a little cumbersome with the elements of

higher atomic number and since only the electrons in the outer ring usually participate in chemical reaction, the briefer symbols shown previously are more commonly used.

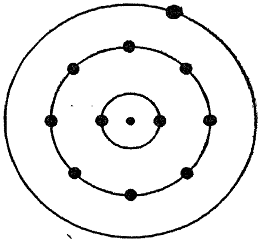


FIG. 14.

The Hydrogen Molecule.—Up to this point, we have treated only isolated atoms. Let us consider what would occur if two atoms of hydrogen approached one another. At relatively great distances, nothing would happen, but as the distance between the atoms grew progressively smaller, a point would be approached when the two nuclei would be so close that each would influence the motion of the electron surrounding the other nucleus. The aberrations in the motion of the electrons will become greater and greater, and the electrons will soon be driven into new orbits, in which they circle both nuclei (see Fig. 15). This picture may also be considered from the Schroedinger point of view, where the orbits now become electrical clouds (Fig. 16). In following the briefer symbolism used previously, the hydrogen molecule would appear as

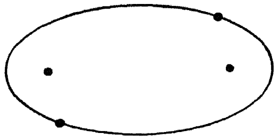


FIG. 15.—Hydrogen molecule.

FIG. 16.—Hydrogen molecule: Schroedinger picture.

H : H
Hydrogen molecule

In this case, the electrons belong to both nuclei; as can be seen in Fig. 17, the hydrogen molecule resembles the helium atom in that both have

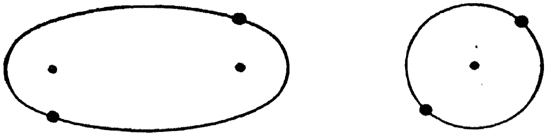
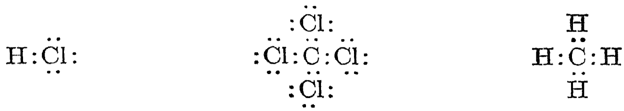


FIG. 17.

two electrons in their outer ring. The arrangement of the electrons about the nucleus in rare gases is peculiarly stable, and all atoms tend to arrange themselves so that they may assume arrangements as similar

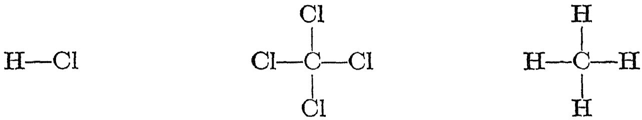
to these elements as possible. Hydrogen at room temperature is completely in the form of diatomic molecules, whereas helium, neon, and the other rare gases exist in the monatomic state.

The Homopolar Bond.—The type of bond that exists between two atoms of hydrogen is called the homopolar or nonpolar bond. This type of bond may also exist between dissimilar atoms, as in hydrogen chloride, carbon tetrachloride, methane, etc.



Hydrogen chloride — Carbon tetrachloride — Methane

This type of bond is often represented by a single line.



Hydrogen chloride — Carbon tetrachloride — Methane

The Heteropolar Bond.—A second type of bond is called the heteropolar bond. If two atoms approached each other, as previously described but in this case had different attractive power for electrons, the atom with the greater attraction for an electron would remove it from the atom with the lesser attraction. For example, if one atom of lithium, with a lone electron in its outer ring, which is rather loosely held, approached an atom of chlorine with seven electrons in its outer ring, rather firmly bound, the lithium atom would lose its electron to the chlorine atom, giving a positively charged lithium ion and a negatively charged chloride ion.

$$[\mathrm{Li}\cdot]^0 + [\cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:]^0 \rightarrow [\mathrm{Li}]^+ + [:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:]^-$$

These ions now have a structure similar to that of the rare-gas atoms and have no electron orbits in common. They therefore behave as individuals, are free to travel around, and are called ions (which is Greek for "wanderers"). Of course, they are somewhat restricted in their perambulations by their electrostatic charges, which cause them to attract oppositely charged ions and also neutral atoms. This type of linkage is the salt-forming, or heteropolar, or, simply, polar type of linkage.

The Semipolar Bond.—There is another type of bond of a different origin, which is somewhat intermediate in character between these

two types; this is the semipolar bond. We may again consider the case of two atoms approaching each other, but in this case, one of the atoms possesses a pair of unused electrons (called a lone pair) and the other needs two electrons to form a stable configuration. Here the atoms may share the pair of electrons (coming from one atom). A case of this type occurs in the reaction of ammonia and hydrogen ion. Ammonia has a lone pair of electrons, whereas hydrogen ion has none. They therefore share the pair of electrons, forming an ammonium ion. The whole ammonium ion now has the charge previously held by the hydrogen ion.

$$\begin{array}{ccc} \mathrm{H} & & \mathrm{H} \\ \mathrm{H}:\ddot{\mathrm{N}}:\mathrm{H} + \mathrm{H}^{+} & & \mathrm{H}:\ddot{\mathrm{N}}:\mathrm{H} \\ & & \mathrm{H} \end{array}$$

Lone pair

Semipolar bonds also exist in neutral molecules, as in the product of the reaction of ammonia with boron trifluoride.

$$\begin{array}{ccccc} \mathrm{H} & & :\ddot{\mathrm{F}}: & & \mathrm{H}:\ddot{\mathrm{F}}: \\ \mathrm{H}:\ddot{\mathrm{N}}: & + & \mathrm{B}:\ddot{\mathrm{F}}: & \rightarrow & \mathrm{H}:\ddot{\mathrm{N}}:\ddot{\mathrm{B}}:\ddot{\mathrm{F}}: \\ \mathrm{H} & & :\ddot{\mathrm{F}}: & & \mathrm{H}:\ddot{\mathrm{F}}: \end{array}$$

Dipoles.—In this type of molecule, one end has a greater negative charge than the other end, the molecule itself remaining neutral. A molecule of this type is said to possess a **dipole.** If molecules having dipoles are placed between two oppositely electrically charged plates, they arrange themselves so that their positive ends face the negative plate and their negative ends face the positive plate. This polarity of many molecules is important in explaining some of their properties.

Valence.—These three types of bonds are called the primary valence[1] forces that exist between atoms. Homopolar and semipolar bonds are called covalence, and heteropolar bonds are called electrovalence. For instance, the ammonium ion NH_4^+ has four covalences and one electrovalence; *i.e.*, the hydrogen atoms are held by covalences, and the positive charge, the electrovalence, enables the ion to attract a negative ion. Similarly, carbon dioxide, CO_2, has two covalent bonds; the carbonate ion $CO_3^{=}$ has three covalent bonds and two electrovalences; hydrogen chloride, HCl, has one covalent bond; the hydronium ion H_3O^+ has three covalent bonds and one electrovalence; the sulfate ion $SO_4^{=}$ has four covalent bonds and two electrovalences, etc.

[1] Secondary valence forces are the attraction due to van der Waals' forces.

Valence Number.—The valence-number concept is purely formal. It evolved independently (of the covalence, electrovalence idea) from the old valence theory. In this concept, certain key elements are assigned positive or negative numbers. The valence numbers of all other elements in molecules can then be calculated by addition and subtraction. For instance, in sodium carbonate, Na_2CO_3, oxygen, O, is assigned a valence number of −2, sodium a valence number of +1, therefore

$$[3(-2)] + \qquad\qquad = -4$$

Since the molecule is neutral, the valence number of carbon is +4. Other examples are:

Sodium sulfate, Na_2SO_4

$$[4(-2)] + [2(+1)] = -8 + 2 = -6 \text{ therefore sulfur} = +6$$

Potassium sulfite, K_2SO_3

$$[3(-2)] + [2(+1)] = -6 + 2 = -4 \text{ therefore sulfur} = +4$$

Sodium sulfide,

$$\text{Na} = [2(+1)] = +2 \quad \text{therefore sulfur} = -2$$

Sodium thiosulfate, $Na_2S_2O_3$

$$] = -6 + 2 = -4$$

$$\text{therefore } S_2 = +4 \quad \text{or} \quad S = +2$$

Sodium permanganate, $NaMnO_4$

$$[4(-2)] + (+1) = -8 + 1 = -7 \text{ therefore Mn} = +7$$

Hydrogen chloride, HCl

$$H = +1 \qquad \text{therefore Cl} = -1$$

Methane, CH_4

$$H_4 = 4(+1) = +4 \quad \text{therefore C} = -4$$

Chloromethane, CH_3Cl
(methyl chloride)

$$[3(+1)] + [1(-1)] = +2 \quad \text{therefore C} = -2$$

Carbon tetrachloride, CCl_4

$$Cl_4 = 4(-1) = -4 \quad \text{therefore C} = +4$$

Chloroform, $CHCl_3$

$$[3(-1)] + (+1) = -2 \quad \text{therefore C} = +2$$

Dichlormethane, CH_2Cl_2

$$[2(-1)] + [2(+1)] = -2 + 2 = 0 \text{ therefore C} = 0$$

The valence number of carbon in the last five compounds varies from +4 through 0 to −4, but the number of covalent bonds is the same in all cases, four, and there are no electrovalences. This last example shows the artificiality of this concept, but it is nevertheless of some use.

NOMENCLATURE

Chemical compounds are named in a variety of ways. Compounds, which have been known since olden times have "trivial" names, which may or may not be commonly used at present. For instance, salt for sodium chloride, sal ammoniac for ammonium chloride, soda ash for anhydrous sodium carbonate, Glauber's salt for sodium sulfate decahydrate, Epsom salt for magnesium sulfate heptahydrate, etc., are names still in use. There are also other compounds whose "trivial" names are not used at present to any great extent, such as aqua fortis for nitric acid, marine acid for hydrochloric acid (although muriatic acid is still used), white vitriol for zinc sulfate, (although blue vitriol is still used for copper sulfate), etc.

Another type of name used is the common chemical name that may or may not be the same as the systematic name. For instance, the common chemical name for $NaHCO_3$ is sodium bicarbonate, and the systematic name is primary sodium carbonate. These common chemical names are those most usually employed in chemistry, especially in dealing with the simpler compounds. However, when the more complicated compounds are encountered, more systematic methods of nomenclature are employed. The principles used in naming the simpler compounds will be outlined here; the more complex compounds will be treated in the next chapter.

Two-element compounds are named by using the name of the element having the positive valence number followed by the root of the name of the element having the negative valence number plus the ending *-ide*, as

Calcium oxide..............	CaO	
Lithium fluoride............	LiF	
Calcium chloride............	$CaCl_2$	
Hydrogen chloride..........	HCl	
Hydrogen sulfide...........	H_2S	
Aluminum chloride..........	$AlCl_3$	
Lithium hydride............	LiH	here $H = -1$ (experimentally)

If the positive element has two valence numbers, the root of the name of the element with the lower positive valence number is given the suffix *-ous*, the higher, the suffix *-ic*, as

Ferrous chloride	$FeCl_2$	Fe = +2
Ferric chloride	$FeCl_3$	Fe = +3
Cuprous chloride	Cu_2Cl_2	Cu = +1
Cupric chloride	$CuCl_2$	Cu = +2
Stannous chloride	$SnCl_2$	Sn = +2
Stannic chloride	$SnCl_4$	Sn = +4
Cerous oxide	Ce_2O_3	Ce = +3
Ceric oxide	CeO_2	Ce = +4

When two elements form a series of compounds, the prefixes *mono-*, *di-*, *tri-*, etc., are added to the name of the element of negative valence number. This is usually done in the case of covalent compounds and less frequently in the case of electrovalent compounds, as

Titanium dichloride	$TiCl_2$	Ti = +2
Titanium trichloride	$TiCl_3$	Ti = +3
Titanium tetrachloride	$TiCl_4$	Ti = +4
Sulfur monochloride	S_2Cl_2	S = +1
Sulfur dichloride	SCl_2	S = +2
Sulfur tetrachloride	SCl_4	S = +4

Sometimes both systems are combined or mixed, as

Nitrous oxide	N_2O	N = +1
Nitric oxide	NO	N = +2
Nitrogen trioxide	N_2O_3	N = +3
Nitrogen dioxide	NO_2	N = +4
Nitrogen tetroxide	N_2O_4	N = +4
Nitrogen pentoxide	N_2O_5	N = +5
Arsenous chloride Arsenic trichloride	$AsCl_3$	
Arsenic chloride Arsenic pentachloride	$AsCl_5$	

Three-element compounds are named on the basis of their acids. To the root of the name of the negative radical is added the suffix *-ous* or *-ic* (to denote lower and higher valence numbers, respectively) and if required the prefix *hypo-*, meaning "less," or *per-*, meaning "more." In the two-element acids,[1] the negative element takes the prefix *hydro-* and the suffix *-ic*, as

HCl	Hydrochloric acid	Cl = −1
$HClO$	Hypochlorous acid	Cl = +1
$HClO_2$	Chlorous acid	Cl = +3
$HClO_3$	Chloric acid	Cl = +5
$HClO_4$	Perchloric acid	Cl = +7
H_2S	Hydrosulfuric acid	S = −2
$H_2S_2O_4$	Hyposulfurous acid	S = +3
H_2SO_3	Sulfurous acid	S = +4
H_2SO_4	Sulfuric acid	S = +6

[1] See later chapter. Hydrochloric acid should really be written $H_3O^+Cl^-$.

(Many of these acids may be unknown in a free state, but their salts are known.) To name the salts, the *-ous* suffix of the acid is replaced by *-ite* and the *-ic* suffix by *-ate;* the word acid is omitted, and the name of the positive element is used before that of the negative element, as

Na_2S	Sodium sulfide[1]
$Na_2S_2O_4$	Sodium hyposulfite
Na_2SO_3	Sodium sulfite
Na_2SO_4	Sodium sulfate
$NaCl$	Sodium chloride
$NaClO$	Sodium hypochlorite
$NaClO_2$	Sodium chlorite
$NaClO_3$	Sodium chlorate
$NaClO_4$	Sodium perchlorate

[1] Two element compounds are, of course, named as in the preceding sections.

If two positive elements replace the hydrogen in an acid, then both names are used, with the prefixes *di-* and *tri-*, if necessary.

	Disodium potassium phosphate
	Sodium potassium tartrate

If only one of the hydrogen ions in the acid is replaced by a positive ion, then the word primary precedes the rest of the name; if two, the word secondary, etc.:

$NaHCO_3$	Primary sodium carbonate
Na_2CO_3	Secondary sodium carbonate
$NaHSO_4$	Primary sodium sulfate
Na_2SO_4	Secondary sodium sulfate
	Primary sodium phosphate
	Secondary sodium phosphate
Na_3PO_4	Tertiary sodium phosphate
$Ca(H_2PO_4)_2$	Primary calcium phosphate

One other point must be considered. Oxygen acids are often formed by the reaction of the oxide with water. The number of molecules of water that are added to each molecule of oxide determine which acid will be formed. To illustrate this point, use will be made of the old Berzelius method of writing formulas. Here the prefixes *meta-*, *pyro-*, and *ortho-* give, in increasing order, the degrees of hydration of the acid.

$P_2O_5 \cdot H_2O \equiv H_2P_2O_6 \equiv 2HPO_3$	Metaphosphoric acid
$NaPO_3$	Sodium metaphosphate
$P_2O_5 \cdot 2H_2O \equiv H_4P_2O_7$	Pyrophosphoric acid
$Na_2H_2P_2O_7$	Secondary sodium pyrophosphate
$P_2O_5 \cdot 3H_2O \equiv H_6P_2O_8 \equiv 2H_3PO_4$	Orthophosphoric acid
	Tertiary sodium orthophosphate

$P_2O_3{\cdot}H_2O \equiv H_2P_2O_4 \equiv 2HPO_2$...	Metaphosphorous acid
$NaPO_2$...	Sodium metaphosphite
$P_2O_3{\cdot}2H_2O \equiv H_4P_2O_5$...........	Pyrophosphorous acid
$Na_2H_2P_2O_5$........	Secondary sodium pyrophosphite
$P_2O_3{\cdot}3H_2O \equiv H_6P_2O_6 \equiv 2H_3PO_3$.	Orthophosphorous acid
Na_3PO_3...........	Tertiary sodium orthophosphite

Unfortunately, inorganic nomenclature has inherited a mass of usages that tend somewhat to confuse the naming of compounds. There is little coordination in the naming of the compounds of many elements. For instance, in chloric acid, $HClO_3$, an *-ic* acid, chlorine has a valence number of +5, whereas in sulfuric acid, H_2SO_4, another *-ic* acid, sulfur has a valence number of +6, and in stannic acid, H_2SnO_3, tin has a valence number of +4. However, the rules given above hold in any given series of acids.

READING REFERENCES

LATIMER, W. M., and J. H. HILDEBRAND: "Reference Book of Inorganic Chemistry," The Macmillan Company, New York, 1940.

MARK, H.: "Physical Chemistry," Interscience Publishers, New York, 1940.

PAULING, L.: "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

QUESTIONS

1. Draw a symbolic picture showing the whole electronic structure of fluorine, calcium, and potassium.

2. Draw a symbolic picture of the structure of ammonium sulfate, and name the various types of bonds.

3. What is the valence number of carbon in the following compounds: CO_2, CO, C_3O_2, C_4H_9Cl, C_6H_5Br?

4. Draw the symbolic picture of the structure of phosphine, PH_3. Would the compound be a dipole? If so, indicate the negative and positive portions of the molecule.

5. Draw a symbolic picture of an actual compound that has a covalent bond; an electrovalent bond; a semipolar bond.

6. List the number of covalent and electrovalent bonds in each of the following substances: IO_4^-, PO_3^-, $P_2O_7^{\equiv}$, $Cr_2O_7^{=}$, SO_3Cl^-, PCl_5.

7. Draw a picture of the electronic structure of the iron atom, showing all the electrons and indicating the valence electrons.

8. Write the formulas and give the systematic names of all the acids that are derived from As_2O_3, arsenous oxide, and As_2O_5, arsenic oxide.

9. Using the chlorine acids as an example, write the formulas and name all the hypothetical acids of fluorine.

10. Given that $KMnO_4$ is potassium permanganate, what are the names of the following manganese compounds: Na_2MnO_4, $NaKMnO_3$, $HMnO_2$, H_2MnO_2?

11. Name the following compounds systematically: $K_2H_2Sb_2O_7$, $NaK(NH_4)PO_4$, Na_2HAlO_3, $NaAlO_2$, K_2Se.

12. Write the formulas of the following compounds: potassium perbromate, secondary sodium orthophosphite, arsenic pentaiodide, lead dioxide, silver cyanate.

CHAPTER IV

COMPLEX IONS AND MOLECULES

Before we can predict, even in part, what the outcome of any reaction will be, we must possess an adequate knowledge of the participating components. We must, therefore, study not only the simple elements and compounds but also the more complex molecules, where the various atoms are linked by different types of bonds. Such molecules have traditionally been called complex ions and complex compounds. May we add, however, that the term complex does not necessarily mean complicated but is rather a generic term.

Let us first consider an experiment that has been performed by many generations of students. When an excess of ammonium hydroxide is added to a solution of copper sulfate, the pale blue solution changes to a deep azure blue. Evidently a reaction has occurred. This reaction gives rise to two questions: (1) what has happened, and (2) can it be utilized? The practical man neglects the first question but investigates the possibilities of the second. The technologist, in his study of this second question, has discovered that such solutions have the property of dissolving cellulose and has used it to produce artificial silk. The analyst, noting that this intense and characteristic coloration invariably occurs whenever a soluble cupric salt is present, uses it as a simple test. The scientist, however, prompted by his enlightened curiosity, looks for the answer to the first question: what has happened? By analysis, he finds that a compound has been formed that is composed of the cupric ion, four ammonia (NH_3) molecules, and whatever anion the solution originally contained. On further examination, the scientist finds that the four ammonia molecules are combined with the cupric ion, forming a new ion whose properties differ markedly from those of the original cupric ion.

Occurrence.—These peculiar types of ions, far from being rare in chemical reactions, are, on the contrary, so widely encountered that an understanding of their behavior provides a satisfactory explanation for many phenomena that disturbed and bewildered the earlier investigators. As an example, let us consider the separation of copper and cadmium ions, which is commonly used in analytical procedures. A solution containing both species of ions, if treated with hydrogen

sulfide, would lead to the formation of both cupric sulfide, CuS, and cadmium sulfide, CdS. Of the two sulfides, cupric sulfide is very insoluble and would therefore precipitate before and more completely than cadmium sulfide. If the experiment is repeated, with the addition of a slight excess of cyanide ion, CN^-, before the saturation with hydrogen sulfide, a yellow precipitate of pure cadmium sulfide would be formed.

This fact would appear utterly confusing if we did not know that both cadmium and copper ions form complex ions with cyanide ion. However, the cadmium complex is less stable than the copper complex and yields, in solution, a cadmium ion which combines with the sulfide ion, forming the characteristic yellow cadmium sulfide.

Structure of Complex Ions.—This experiment illustrates how complex ion formation can be used to make certain reactions understandable. We now propose to examine critically some complex ions in order to gain a deeper insight into their structure or, to put it differently, their atomic and electronic architecture. If the student considers the complex ions mentioned thus far, he cannot deny being confused. His reasoning would run somewhat like this: I understand the mechanism that leads to the two positive charges on the cupric ion. The copper has lost two electrons to chlorine or some other element and therefore possesses two positive charges. In the ion $Cu(NH_3)_4^{++}$, the ionic charge is the same as in the original ion. What factors, then, cause the four molecules of ammonia to attach themselves to the cupric ion?

Whenever, in the study of natural phenomena, facts are encountered that do not fit into current patterns of thought, we can do one of two things: (1) ignore the recalcitrant facts or (2) insist on finding an explanation. The latter alternative often demands that we discard some of these patterns and replace them with newer models.

Complex ions were largely ignored until the beginning of this century, when Alfred Werner singled them out and made them the object of a very exhaustive investigation. After studying all the available facts, Werner arrived at an interpretation of the structure of complex compounds. Let us follow Werner's reasoning with a definite example, hexamminocobaltic chloride, $[Co(NH_3)_6]Cl_3$. The cobalt, says Werner, may be thought of as a sphere surrounded by a field of force. Let us assume that the six ammonia molecules are attracted to the "central atom" (cobalt, in this case) and since they are subjected to exactly the same attraction will distribute themselves symmetrically around the cobalt. If we imagine the latter to be the center of an octahedron, each NH_3 would be located at one of the corners. The six

molecules of ammonia are now held by the "central atom" in the first sphere of influence. The "central atom," in addition to holding the six ammonia molecules in its first sphere, has a second sphere of influence wherein it can hold three chloride ions.

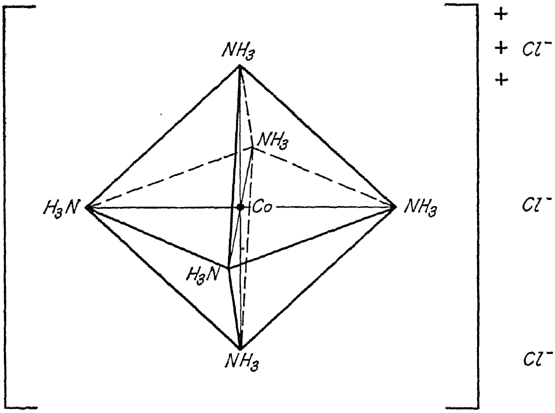


FIG. 18.—Hexamminocobaltic chloride.

We may ask at this point why Werner insisted on placing the six molecules of ammonia in the corners of a well-defined geometric figure? This question may be answered by saying that a good theory should provide more than a mere explanation. It should also enable us to predict the related phenomena.

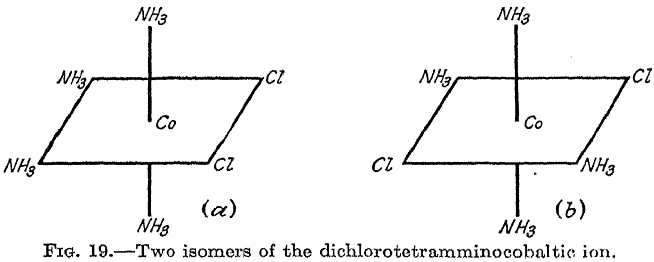


FIG. 19.—Two isomers of the dichlorotetramminocobaltic ion.

If we replace two of the six ammonia molecules with chloride ions (this has been done experimentally), we should obtain two compounds that differ, at least in some of their physical properties: solubility, color, etc. We should expect this because in Fig. 19a, the two halogens are close together, whereas in Fig. 19b, they are as far apart as possible.

The actual experimental verification of this prediction emphasizes the importance of this theory.

Coordination Number.—The compound just studied has six ammonia molecules around the cobalt. Werner calls this the **coordination number** of the element and defines it as the number of molecules or ions held in the first sphere of influence. Upon examining numerous complex compounds, we find that 6 is by far the most frequently encountered coordination number. In our familiar example, $Cu(NH_3)_4^{++}$, copper has a coordination number of 4, whereas in $Ag(NH_3)_2^{+}$, silver has a coordination number of 2 and tungsten in $W(CN)_8^{-4}$ has a coordination number of 8. This suggests a reference to the periodic table and leads to the question, does the coordination number vary with the size of the atom and the atomic volume? It is not surprising, indeed, to find that carbon, nitrogen, and boron, *i.e.*, elements of small atomic volume, never exceed a coordination number of 4, whereas molybdenum, to mention but one element of considerable size, exhibits a coordination number of 8 in $K_5Mo(CN)_8$.

Theory and Hypothesis.—Before proceeding to a modern elaboration of Werner's theory, it may be instructive to pause briefly to consider what is meant by "theory" and "hypothesis" and to consider their function and virtues in science. Facts may be compared to bricks. Bricks are useful in building a house, but a pile of bricks is not a house. Similarly, a mass of observations must be arranged into a pattern before it is called a hypothesis. The hypothesis becomes a theory upon growing older and proving its value in predicting new facts. It gains in prestige and gets promoted. Theories often reach such a venerable age that they outlive their usefulness, like the human executive who has lived to be a great asset to his firm but now is aged and is resting on his laurels. His past prestige, unfortunately, prevents a more vigorous and active person from taking his place. This suggests the function of theories in science. True, a theory coordinates a large number of facts and impresses a meaning on the pattern thus found, but its main purpose consists in stimulating research to discover new facts. A theory that has lost this tonic effect should be discarded. Werner's theory proved to be one of the most vivifying influences in inorganic chemistry. This should not, however, blind us to its limitations. We should like to know, for example, why six apparently neutral molecules were attracted to the metal ion in the first place? What mysterious force attracted them and held them at equal distances from the central atom?

Modern Interpretation of Werner's Theory.—In searching for the causes that bring about complex ion formation, let us consider first

the finer structure of ammonia. We have previously seen that this molecule may be represented as $\begin{array}{c}\mathrm{H}\\ \cdot\cdot\\ :\mathrm{N}:\mathrm{H}.\\ \cdot\cdot\\ \mathrm{H}\end{array}$ We note that three of the nitrogen valence electrons are utilized in forming covalent bonds, leaving a pair of electrons unengaged. Let us call this pair a lone pair of electrons. It should not be difficult to realize that, although the sum of the negative charges is counterbalanced by the same number of positive charges and hence the molecule as a whole is neutral, the distribution of charges is nevertheless unsymmetrical. The result is to produce in the molecule a negative pole and a positive pole, the former

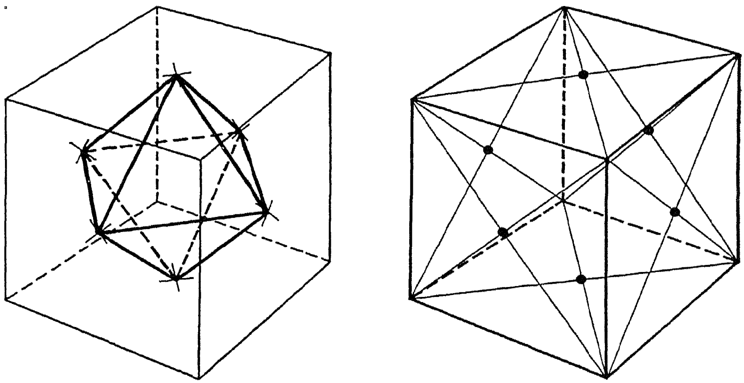


FIG. 20.—Octahedron inscribed in a cube.

being centered in the region of the lone pair. Molecules of this type are called dipoles.

Let us now consider how this concept is related to the structure of the hexamminonickelous ion $Ni(NH_3)_6^{++}$. Before doing this, we must examine the finer structure of the nickel ion. Nickel has an atomic number of 28, but since we are dealing with the nickelous ion that has lost two electrons from the *N* shell, we have, actually, 26 electrons, 8 of which are on the third sublevel of the *M* shell and hence find themselves at the outpost of the atom. Let us imagine that they occupy the corner positions of a cube.

There is no necessity at all to assume that the electrons remain in a rigidly fixed position; it suffices to admit that the negative charge is concentrated at the corners of the cube. If we visualize the distribution of electrical charges on a face of this cube, we can readily see that the more one moves away from a corner the less negative the charge becomes, until, upon reaching the center of the face, the charge

becomes a minimum. In addition, we should remember that the positive charge of the atomic nucleus is exerting its maximum action at this same point. Since a cube has six faces, there are six points of fractional positive charge. The six points are at equal distances from the center of the atom and, indeed, define an octahedron. We have thus returned to Werner's theory, but now we understand why the six dipoles (NH_3 in our example) would tend to attach themselves with their negative pole (the lone pair) to the six fractional positive regions around the central atom.

This can be illustrated by a structural formula in which, for the sake of clarity, only the strategic electrons have been drawn (Fig. 21).

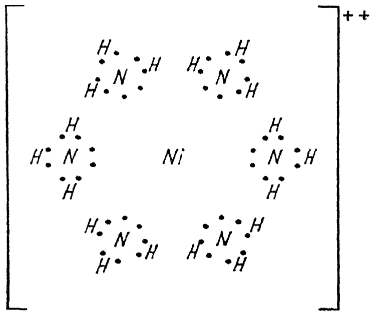


FIG. 21.—Symbolic representation of the hexamminonickelous ion.

It is apparent that in such a case each coordinated molecule shares its lone pair of electrons with the central ion. In the Sidgwick concept, each coordinating molecule "donates" its lone pair of electrons to the central ion. This sharing creates a bond, variously designated as semipolar bond or coordinate link, and is often represented by an arrow pointing from the electron pair to the receiving central ion. This concept is a help to the imagination and therefore useful, but the student should not be led to a belief in the actual existence of one-way traffic signs in the make-up of complex ions.

Types of Complexes.—In the light of this explanation, we should now investigate the often expressed idea that "inorganic chemistry deals with a comparatively small number of well-defined compounds, most of which have been exhaustively studied." The fallacy of this view is easily demonstrated. Let us select a single ion, *e.g.*, Co^{+++}, having a coordination number of 6 and thus having six positions to be filled with dipole molecules such as NH_3, pyridine, water, NO, etc., or with anions such as halide, NO_2^-, CN^-, etc. We proceed now to combinations, *e.g.*

$$\begin{array}{ccc} & NH_3 \; H_2O & \\ NH_3 & Co & Cl \\ & NH_3 \; NO_2 & \end{array} \qquad \left[\begin{array}{ccc} & NO_2 & \\ NO_2 & & Cl \\ & Co & \\ NO_2 & & H_2O \\ & Cl & \end{array}\right]^{=} \qquad \left[\begin{array}{ccc} & Br & \\ NO_2 & & Cl \\ & Co & \\ NH_3 & & NO_2 \\ & NH_3 & \end{array}\right]^{-} \qquad \left[\begin{array}{ccc} & H_2O & \\ NH_3 & & H_2O \\ & Co & \\ CN & & H_2O \\ & CN & \end{array}\right.$$

$$\left[\begin{array}{ccc} & NO & \\ NH_3 & & CN \\ & Co & \\ NH_3 & & NH_3 \\ & NO & \end{array}\right]^{++} \qquad \left[\begin{array}{ccc} & Cl & \\ NH_3 & & NH_3 \\ & Co & \\ Cl & & NH_3 \\ & Cl & \end{array}\right]^{0} \qquad \left[\begin{array}{ccc} & Cl & \\ Cl & & Cl \\ & Co & \\ Cl & & Cl \\ & Cl & \end{array}\right.$$

We can readily see that the number of possible complex ions and complex compounds becomes quite large. Consider, too, that thus far we have confined ourselves solely to cobalt compounds. If we varied the coordinating ion as well as the groups of molecules and ions, we should produce practically an unlimited number of compounds. The successive replacement of dipole molecules such as H_2O by anions such as Cl^- deserves further comment.

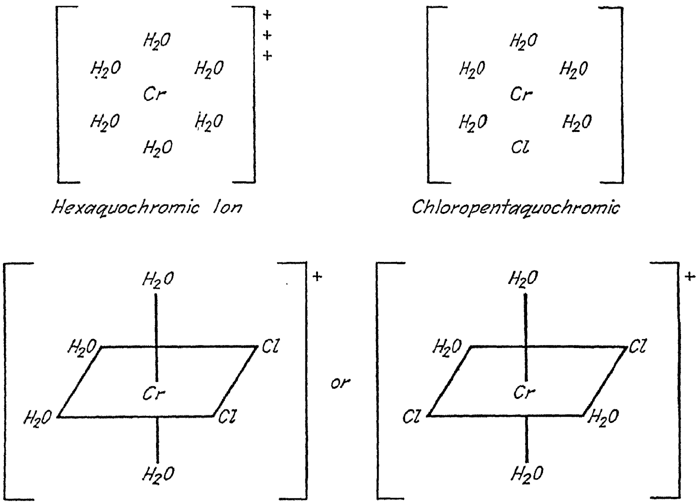
Let us consider chromic chloride hexahydrate, a compound characterized by a beautiful violet color due to the complex hexaquochromic ion $Cr(H_2O)_6{}^{+++}$. We could easily determine that the solution contains three chloride ions for each complex ion. This we could do, for example, by adding silver nitrate solution and weighing the silver chloride precipitate formed. Let us now exchange a Cl^- for a molecule of H_2O, thus producing the chloropentaquochromic ion $[Cr(H_2O)_5Cl]^{++}$. (The practical details of the preparative procedure need not concern us here.) We see first that the charge of the complex ion has dropped from plus 3 to plus 2. The explanation is readily forthcoming. The incorporation of a negative ion in the first sphere of influence uses one of the electron pairs of the ion, thus forming a coordinate link. However, the negative charge on the chloride ion remains. Therefore, the total charge on the ion is composed of plus 3 from the chromium and negative 1 from the chloride, leaving a net charge of plus 2. This change has definitely altered the complex ion. The color of the solution now is deep green. By adding a solution of $AgNO_3$ to this solution, we could prove the presence of 2 Cl^- for each complex ion. A further exchange of Cl^- for H_2O would yield the dichlorotetraquochromic chloride $[Cr(H_2O)_4Cl_2]Cl$, a light green compound.

As a further illustration, let us use hexamminocobaltic chloride and successively replace the ammonia molecules with the monovalent

nitrite ion. The numerical value under each formula represents the conductivity of a $0.002N$ solution of each compound.

$[Co(NH_3)_6]^{+++}\ 3Cl^-$	$[Co(NH_3)_5(NO_2)]^{++}\ 2Cl^-$
412	240
$[Co(NH_3)_4(NO_2)_2]^+\ Cl^-$	$[Co(NH_3)_3(NO_2)_3]^0$
97	1.5
$[Co(NH_3)_2(NO_2)_4]^-\ K^+$	$[Co(NO_2)_6]^{\equiv}\ 3K^+$
97	418

Note that the conductivity decreases sharply with the decrease in positive charge. The compound $Co(NH_3)_3(NO_2)_3$ is neutral. Complexes of this type are soluble in organic solvents such as chloroform, carbon tetrachloride, etc. Further exchange of ammonia and nitrite



Dichlorotetraquochromic Ion (two forms)

FIG. 22.

ions imparts a negative charge and transforms the complex into a complex anion. Consequently the conductivity increases and reaches a maximum with the hexanitritocobaltate ion $[Co(NO_2)_6]^{\equiv}$, the end product of our series of substitutions.

Stability of Complexes.—It is to be expected that the stability of complex ions and complex compounds will vary considerably. $Co(NH_3)_6^{+++}$ is remarkably stable, whereas the corresponding cobaltous compound $Co(NH_3)_6^{++}$ dissociates to a considerable extent in

solution. This may appear surprising and suggests the question, is it possible to predict, at least qualitatively, whether a given complex ion will prove stable or not? Such predictions are made possible by the hypothesis of the **effective atomic number, E.A.N.** We recall that "atomic number" refers to the number of positive charges of an atomic nucleus, which number also coincides with the number of electrons surrounding such a nucleus. "E.A.N." refers to the total number of electrons surrounding the central atom of the complex. This is best illustrated with a simple example. Let us assume that we wish to determine the effective atomic number of copper in $Cu(NH_3)_4^{++}$. The atomic number of copper is 29, which tells us that 29 electrons surround the nucleus in the neutral copper atom. In the cupric ion, however, the electrons belonging to copper are $29 - 2 = 27$. To this must be added 8 electrons emanating from the 4 electron pairs directly coordinated in making up the complex. Therefore the E.A.N. of the complex ion is $27 + 8 = 35$.

The hypothesis now states that whenever the effective atomic number of a complex ion coincides with the atomic number of a rare gas, we can expect greater stability than when it does not. As an example, let us choose the ferrocyanide ion, a well-known stable complex. Its systematic name is hexacyanohypoferrite ion. The effective atomic number of the iron in the compound equals 36. (Atomic number of $Fe = 26 - 2 = 24$ for the atomic number of ferrous ion $+12$ for the six CN groups $= 36$.) The rare gas krypton has an atomic number of 36. It follows that the ferrocyanide complex should be found stable, a fact that can be demonstrated by purely experimental methods. Now let us take an unstable complex, the hexamminocobaltous ion, mentioned previously. The effective atomic number of cobalt in this complex is 37, which does not coincide with a rare-gas atomic number. We should therefore predict instability, which again is actually found experimentally. However, hexamminocobaltic ion is stable, since the effective atomic number of cobalt is 36, coinciding with the atomic number of krypton.

Thus far we have concerned ourselves with the general aspects of the complex-ion problem, their structure, formation, and stability. Our next task is comparable to that of Ali Baba, who found himself in the treasure cave amidst unending rows of gold pieces and jewels. He was faced with the difficult task of choosing which of the treasures to carry off with him. In attempting to record and describe some interesting examples of complex ions, we must choose from a wealth of material of which only a specialist can hope to keep track. It seems wise, therefore, under the circumstances, to refer the more inquisitive student to some excellent treatises on the subject (a list of which will

be found at the end of this chapter) and otherwise to content ourselves with recording a few examples of particular interest to the analyst.

Ammonia Complexes.—To this class belong many compounds used in qualitative analysis either for identification purposes, as the intense blue $Cu(NH_3)_4^{++}$ (tetrammino cupric ion) or for separations, as $Ag(NH_3)_2^+$ (diamminoargentic ion). The latter is formed whenever silver chloride is treated with ammonia, the silver going into solution and so being removed from any other insoluble chlorides present. A study of the formulas of the complex ions and molecules already mentioned will show that it is the lone electron pair in the ammonia molecule that binds it in complex ions. From this we could predict that the other three electrons need not necessarily be shared with hydrogen atoms but that other atoms or groups of atoms could be substituted for hydrogen.

H	R	R	R
$:\ddot{N}:H$	$:\ddot{N}:H$	$:\ddot{N}:R$	$:\ddot{N}:R$
H		H	R
Ammonia	Monosubstituted ammonia	Disubstituted ammonia	Trisubstituted ammonia

There is a great deal of experimental evidence that this is the case. Consider the formula of pyridine, a liquid of unpleasant odor but of great usefulness. It may be conceived as being derived from ammonia, in which the three electrons are shared with carbon atoms, leaving the lone pair of nitrogen intact.

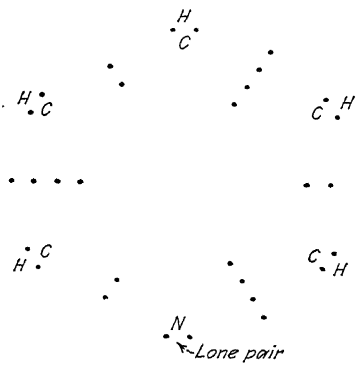


FIG. 23.—Pyridine.

Pyridine, therefore, may be substituted for NH_3 in complex ions. Best known in qualitative analysis are the "pyridonium" complexes of zinc, cadmium, and cobalt. Pyrrole, which is a close relative of pyridine, as can be seen from its formula, leads us to the question, which is the most important chemical compound in the entire realm of nature?

There can be no hesitation about the answer; it is chlorophyll, the green pigment of leaves and grass, a coordination complex in which the central atom, magnesium, is surrounded by four pyrrole nuclei. Is it a mere coincidence that we should encounter complexes so close to the roots of life?

Hydrates and Aquo Complexes.—In one of the preceding paragraphs, we encountered chromic chloride hexahydrate. The fact that

molecules of water function very much like NH_3 molecules as constituents of complex ions is so widely encountered that we often ignore the coordinated water molecules. The three forms of chromic chloride demonstrate, however, that the replacement of a single H_2O in the chromic complex with a chloride ion (as previously discussed) brings about a visible marked change in the properties of the compound.

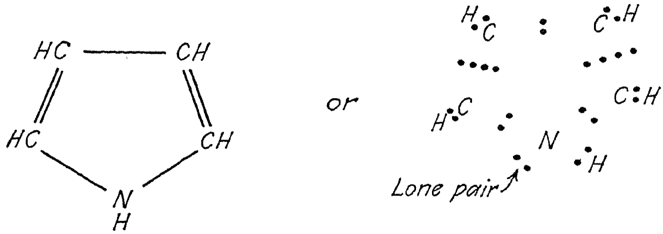


FIG. 24.—Pyrrole.

The original ion $Cr(H_2O)_6^{+++}$ was violet, whereas the resulting $[Cr(H_2O)_5Cl]^{++}$ (pentaquochlorochromic ion) is green. Molecules of H_2O, as we can see, can be constituents of anionic as well as cationic complexes. Whenever entire water molecules are coordinated into complex ions, we speak of hydrates or aquo complexes. We know, however, of instances, by no means rare, in which only the hydroxyl ion is incorporated into cationic complexes, as, for instance, in the pentaquohydroxozinc ion $[Zn(H_2O)_5(OH)]^+$. This ion is found in zinc chloride solutions and accounts for the peculiar properties of such a solution (which will be discussed in greater detail in Chap. VII).

Acido Complexes.—The reader may not be aware of it, but the fact remains that he is already quite familiar with some compounds of this class. Let us recall the successive replacement of ammonia molecules with nitrite ions, starting with $Co(NH_3)_6^{+++}$. From the fourth replacement on, the original cation has been changed into an anion, yielding as the final product $Co(NO_2)_6^{---}$. This ion immediately brings to mind a large number of similarly constituted anions that are often encountered in analytical chemistry. Best known are probably the ferro- and ferricyanide ions, $Fe(CN)_6^{----}$ and $Fe(CN)_6^{---}$, which not only are used as reagents for the detection of iron but are also of great industrial importance in the production of paint pigments. The formula of the mineral cryolite, indispensable in the production of aluminum, is often written as $AlF_3{\cdot}3NaF$. Such "double-salt" formulations should be viewed with suspicion, since they are, as a rule, leftovers from the past, when complex ions were not properly understood. The correct formula for cryolite should, of course,

and its name is trisodium hexafluoraluminate.

The hexafluoroferrite ion, $FeF_6^{=}$ is a good example of a practical application of complex ion formation to analytical procedures. Let us suppose that a certain test is interfered with by the presence of ferric ion. We could, of course, devise a method of converting the iron into some insoluble compound and then filter it off. This, however, would be time-consuming and probably would result in incomplete removal. The addition of fluoride ion offers a much more elegant solution to our problem. The ion would be incorporated into a very stable complex and thus would not interfere with the test.

As our last example, we choose Nessler's reagent. This reagent is indispensable in water analysis in that it enables one to detect minute amounts of ammonia (which, in turn, indicate decaying organic matter). Nessler's reagent is prepared according to the following equations:

$$4K^+ + 4I^- + HgCl_2 \rightarrow 4K^+ + HgI_4^{=} + 2Cl^-$$

It reacts as follows:

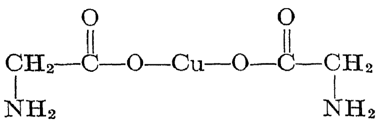
$$2\left[\begin{array}{c} :\ddot{I}: \\ :\ddot{\underset{\cdot\cdot}{I}}:\ddot{Hg}:\ddot{\underset{\cdot\cdot}{I}}: \\ :\underset{\cdot\cdot}{I}: \end{array}\right]^{=} + 3OH^- + \begin{array}{c} N \\ :\ddot{\underset{\cdot\cdot}{N}}:H \\ N \end{array} \rightarrow \underset{\text{Brown precipitate}}{\left[\begin{array}{c} H \\ :\ddot{\underset{\cdot\cdot}{N}}:Hg:\ddot{\underset{\cdot\cdot}{O}}:Hg:\ddot{\underset{\cdot\cdot}{I}}: \\ H \end{array}\right]^{0}} + 7I^- + 2H_2O$$

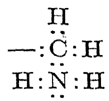
Polyhalides, Polysulfides, and Polyacids.—The student has now acquired the firm conviction that he has gathered all the essential facts pertaining to complex ions and that the remainder of this chapter is merely an elaboration of some details with suitable examples. Nature, however, seems to delight in disappointing the investigator who thinks that he has at last succeeded in smartly classifying a certain set of phenomena. Surrounding the central atom in the first sphere of influence, we have thus far encountered molecules such as NH_3, or H_2O, dipoles, in other words. We also found ions such as Cl^- or CN^-, etc. We now proceed to molecules. It is well known that only minute amounts of iodine dissolve in water. The dark crystals of the element, however, easily dissolve in a potassium iodide solution. The generally accepted explanation assumes the formation of the $(I{\cdot}I_2)^-$ complex. This symbolic representation implies that the iodide ion acts as the central atom binding the molecule of iodine. If, instead of KI, we select CsI solution, a still larger amount of iodine can be dissolved, and the ions found are formulated as

$$Cs^+ \quad \left.\begin{array}{c} \quad I_2 \\ :\ddot{\underset{\cdot\cdot}{I}}: \\ \quad I_2 \end{array}\right]$$

Ammonium polysulfide is another example of such elemental complexes, as we may properly call them. This reagent has the remarkable property of dissolving the sulfides of arsenic, antimony, and tin and is therefore widely used in analytical schemes to effect the separation of the Group II sulfides into subgroups. The student memorizes the formula $(NH_4)_2S_x$ for ammonium polysulfide and seldom gives any thought to the value of x. It should, however, be written as $(NH_4)_2S{\cdot}S_y$, wherein y may vary from 1 to 4.

Inner Complexes or Chelate Compounds.—We would predict without hesitation that whenever NH_3 is added to a solution containing Cu^{++} ion, the complex $Cu(NH_3)_4^{++}$ will form. We now propose to modify slightly this familiar experiment. Instead of cupric ion, suppose that we were dealing with a water-soluble but un-ionized copper compound. Would copper retain its ability to coordinate ammonia molecules? We should find by experiment that it would. Now suppose that the copper compound had somewhere in its molecule an amino group, —NH_2. These conditions would be realized in the following compound:





We see that the amino group —NH_2 has retained the electron distribution of the ammonia molecule. There remains, in particular, the lone electron pair, the indispensable requirement for complex formation. The experiment reveals that copper glycinate forms, indeed, a complex compound, characterized by an intense blue color. The structure of the compound could be represented as follows:

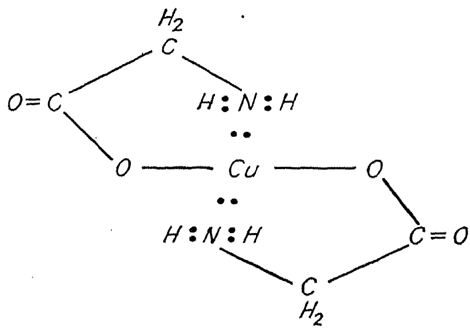
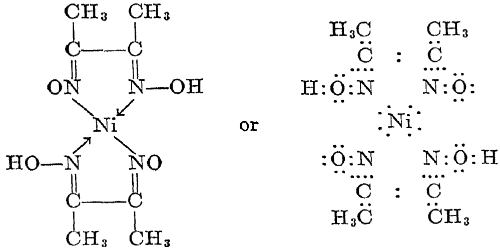


FIG. 25.—Copper glycinate.

It is significant that since both the central metallic atom and the coordinated groups are parts of the same molecule, the complex formation necessitates a "rolling up" or cyclization of the molecule. In our example, two five-membered rings have been formed. The designation "inner complexes" or chelate (*i.e.*, clawlike) compounds seems therefore quite appropriate. The application of most of the organic reagents described in our experimental part is founded on their ability to form such chelate compounds. A typical example is nickel dimethyl glyoxime, which precipitates as a beautiful red compound whenever dimethyl glyoxime is added to an ammoniacal nickel solution. The formula is



APPLICATION OF COMPLEX IONS TO ANALYTICAL PROCEDURES

A certain insight into the general types of complex ions and complex compounds having been gained, it seems appropriate to group such complex ions that are of special interest to the analytical chemist and consider them separately.

1. The extensive use of complex ions and compounds in final identification tests should be stressed. The formation of the intensely colored $Cu(NH_3)_4^{++}$ ion from ammonia and the $Cu(H_2O)_4^{++}$ often suffices definitely to establish the presence of copper. The ferrocyanide ion, $Fe(CN)_6^{----}$, is used as a sensitive reagent for ferric ion, since the two form a deep blue precipitate, Prussian Blue, $Fe_4[Fe(CN)_6]_3$. The frequent use in recent years of organic reagents like diphenyl carbazide, rhodanine, thiosinamine, etc., as confirmatory tests is based on their forming intensely colored complex compounds of the chelate type with particular cations. The distinctive advantages of these reagents are their sensitivity and their specificity. The chelate compounds obtained by these reactions are very often of the nonionic type and hence are easily soluble in organic solvents. This enables us to increase the sensitivity of many tests, since we are thus able to concentrate the final identification product by extraction with a small

volume of an organic solvent. A good example of this is mercuric diphenylcarbazone which can be extracted with a small amount of amyl alcohol to give an intensely blue solution.

2. Complex formation is often utilized in various separation procedures. As a simple example, let us consider the separation of silver chloride and mercurous chloride in the first analytical group. The addition of an ammonia solution to this mixture will result in the solution of the silver chloride because of the formation of the diamminosilver ion, $Ag(NH_3)_2^+$. The mercurous chloride will at the same time be converted to an insoluble mixture of mercury and mercuric amido chloride, $HgNH_2Cl$. Another example is the separation of the sulfides of Group II into two subgroups. The sulfides of arsenic, antimony, and tin are soluble in warm ammonium polysulfide solution, forming the thio complexes; the thioarsenate, $AsS_4^{\equiv}$, the thioantimonate, $SbS_4^{\equiv}$, and the thiostannate, $SnS_3^{=}$, respectively; the sulfides of the other metals in this group remain practically unaffected.

Another important analytical procedure is the separation of cadmium from copper. If a mixture containing the tetramminocupric ion and the tetramminocadmium ion is treated carefully with cyanide ion, the following series of reactions occurs:

$$
\begin{aligned}
2Cu(NH_3)_4^{++} + 4CN^- &\rightarrow 2Cu(CN)_2 + 8NH_3 \\
2OH^- + 2Cu(CN)_2 &\rightarrow \underset{\text{white}}{Cu_2(CN)_2} + CNO^- + H_2O + CN^- \\
Cu_2(CN)_2 + 4CN^- &\rightarrow 2Cu(CN)_3^{=} \\
Cd(NH_3)_4^{++} + 2CN^- &\rightarrow Cd(CN)_2 + 4NH_3 \\
Cd(CN)_2 + 2CN^- &\rightarrow Cd(CN)
\end{aligned}
$$

The cyanocadmium complex is less stable than the cyanocuprous complex; hence when hydrogen sulfide is added, pure cadmium sulfide is precipitated. (For a discussion of the quantitative aspects, see Chap. VIII.)

Lastly, it should be pointed out that complex-ion formation is not invariably a blessing as far as the analyst is concerned. Suppose, to give only one well-known example, that a solution is to be analyzed for aluminum, iron, and chromium. The addition of a slight excess of an ammonia solution would ordinarily suffice to precipitate these three metals as the hydroxides. However, in the presence of many organic acids, such as citric and tartaric acids, the precipitation is partly or completely inhibited because of the formation of citrate or tartrate complexes. This problem can, of course, be solved, but the solution involves the complete destruction of the offending acids by a rather tedious procedure.

OUTLINE OF THE SYSTEMATIC NOMENCLATURE OF COMPLEX COMPOUNDS

1. The name of the cation precedes that of the anion.
2. In naming the coordination complex, the groups are named in the following order:

NOTE: If the name of a coordinated group ends in *-ide*, this ending is replaced by an *-o*; if the name ends in *-ite* or *-ate*, the final *-e* is replaced by an *-o*.

a. **Acid groups:** Cl^-, chloro; Br^-, bromo; $SO_4^=$, sulfato; $CO_3^=$, carbonato; CN^-, cyano; CNO^-, cyanato; NO_2^-, nitrito; etc.
b. **Neutral groups containing oxygen:** H_2O, aquo; $O^=$, oxo; $O_2^=$, peroxo; OH^-, hydroxo; etc.
c. **Ammonia groups:** NH_3, ammino.
d. **Miscellaneous groups:** $S^=$, thio; $NH_2CH_2CH_2NH_2$, ethylene diamino; etc.

NOTE: Each of the preceding groups has a prefix (if more than one is present) denoting the number of such groups in the ion. The prefixes used are *di-*, *tri-*, *tetra-*, *penta*, *hexa-*, etc.

e. The name of the **central or coordinating atom** with the appropriate ending. If the ion is a cation, it has the same ending that the unsubstituted ion would bear. If the ion is an anion, it has the ending of the corresponding anion.

Examples:

$[Co(NH_3)_6]Cl_3$ .... Hexamminocobaltic chloride
$[Cl(H_2O)(NH_3)_4Co]Cl_2$ .... Chloraquotetramminocobaltic chloride
$K[Co(NH_3)_2(NO_2)_4]$ .... Potassium tetranitritodiamminocobaltate
$O)_3]$ .... Tripotassium hexachlorotriaquorhodite
$))_2]$ .... Potassium tetrabromodiaquoaurate

READING REFERENCES

EMELÉUS, H. J., and J. S. ANDERSON: "Modern Aspects of Inorganic Chemistry," 1st ed., D. Van Nostrand Company, Inc., New York, 1940.
MORGAN, GILBERT T., and FRANCIS H. BURSTALL: "Inorganic Chemistry," W. Heffer & Sons, Ltd., Cambridge, England, 1936.
THORNE, P. C. F., and A. M. WARD: "Ephraim's Inorganic Chemistry," 3d ed., Gurney and Jackson, London, 1940.

QUESTIONS

1. What is the coordination number of the copper-ammonia complex formed in analytical Group II*A*? Of the silver-ammonia complex in Group I? Of the zinc-ammonia complex in Group III?

2. What is the coordination number of iron in potassium ferrocyanide, potassium ferricyanide, sodium nitroprusside?

3. What is the E.A.N. of nickel in $[(NH_3)_2(H_2O)_2(NO_2)_2Ni]^+$? In $[(NH_3)_3 \cdot (H_2O)_2(NO_2)Ni]^{++}$?

4. Write the formulas and names of the ions produced by the successive replacement of NH_3 by Cl^- in the hexamminochromic ion.

5. In making sodium nitroprusside from sodium ferricyanide, how do you explain the change in the charge of the anion?

6. Draw pictures of all the possible isomeric forms of the $PtF_4Cl_2^{=}$ ion; of the $PtF_3Cl_3^{=}$ ion.

7. Name the following compounds: $NiSiF_6$, $[(H_2O)_2(NH_3)_4Ni](NO_3)_2$, Na_3AsS_3O, Na_3SbS_4.

8. Write the formula of the following compounds: potassium triiodoplumbite, sodium dibromodinitritodiaquoaurate, dipotassium pentanitritoamminocobaltate.

9. Give the names of the following ions: $FeF_6^{\equiv}$, $Cr(SO_4)_3^{\equiv}$, $Cu(CN)_3^{=}$.

10. Write the formulas of the following compounds: hexafluorosilicic acid, silver dicyanoargentate, trinitritodiaquoamminocobalt.

CHAPTER V

THE KINETIC THEORY OF MATTER

We have all at some time made the observation that substances exist in three physical states: gas, solid and liquid. The question now before us is, what is the correlation between the known facts of atomic and molecular structure and these three states of matter?

In the preceding chapters, we have considered single atoms and molecules, whereas actual substances with which we are familiar are composed of very large numbers of molecules. We must therefore study the effects produced when this condition exists.

Water, for example, can exist in the solid, liquid, or gaseous state, and in each of these states the molecule H_2O remains unchanged. The factors responsible for the physical differences must therefore lie in the forces that act among these large numbers of molecules. We know that the gas, steam, can be quite highly compressed, and since it is not probable that the molecules are themselves compressed, it seems plausible to say that there is a large amount of free space between molecules. Liquids, such as water, and solids, such as ice, are, however, compressible only to a slight extent, and we may therefore conclude that in these latter states the molecules are closer together.

In order to gain a deeper insight into the interplay of forces existing among large numbers of molecules, we must consider these states of matter separately. The simplest case is that of the gases, and we shall therefore study this state first.

GASES

How may a gas be characterized experimentally? One of the criteria of a gas is its lack of shape; *i.e.*, it fills completely any container into which it is placed. The forces of gravity have no apparent effect on gases.[1] This point may be illustrated by the ingenious experiment performed by Dalton in 1801. He connected two bottles, one filled with hydrogen and the other with carbon

[1] The inquisitive student may ask why, if this statement is true, does not the atmosphere surrounding the earth float away. The answer is that gravity does affect gases but to such a small extent that it is unnoticeable as long as experimentally practical quantities are used.

dioxide, with the bottle of hydrogen at the top (Fig. 26). After some time, he removed the connecting tube, stoppered the bottles, and after inverting the bottles in a solution of potassium hydroxide (which absorbs carbon dioxide), removed the stoppers. The liquid rose to the same level in both bottles. This can be explained only if the gases have mixed spontaneously and uniformly. This, in turn, must mean that the molecules of gases are in continuous motion and since this condition of equilibrium was attained with fair rapidity, the molecules must be moving at high velocity.

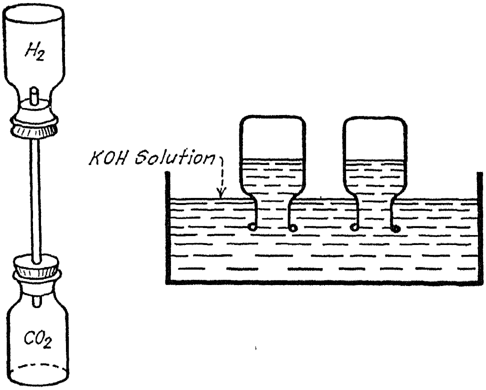


FIG. 26.—Dalton's experiment.

Another criterion of gases is their low density when compared to liquids and solids. For example, 30,600 ml. of water vapor at 100°C. has approximately the same weight as 18 ml. of water at 100°C. A third criterion that we have mentioned previously is high compressibility. All these experimental observations and the phenomena attendant upon them may be explained in terms of the kinetic molecular theory.

The Kinetic Theory.—According to this theory, gases are composed of a swarm of molecules, comparatively far apart, each molecule moving independently of the others at high velocity and in a straight line. The energy of this motion is called the kinetic energy of the gas and depends directly upon the number of molecules, the mass of each, and their average velocity. Since the molecules move in a straight line, it is evident that their paths will change only when they "collide" with other molecules.[1] Or, since the molecules move independently of one

[1] By collision we mean not actual collision but rather that the molecules swerve when they approach one another very closely (see Chap. VI).

another in a straight line, the forces of attraction and repulsion inherent in each molecule evidently have no effect upon each other. This is explained by assuming that the molecules are generally very far apart and that the forces at these distances are too weak to exert any influence. The only exception occurs when molecules undergo collision.

This qualitative picture has been expressed mathematically, and as a result, we are able to make certain useful deductions. We may, for example, calculate the average or mean velocity of a gas molecule. For hydrogen, this is 183,000 cm. per sec., and for oxygen, the value is 46,000 cm. per sec. at S.T.P. It is obvious that each molecule undergoes innumerable collisions in this time. As a matter of fact, the average distance that a molecule travels before it collides with another is about 0.00001 cm. at standard conditions. This value is called the mean free path of the gas. The average distance between molecules at 0°C. and 1 atm. pressure is about thirteen times their diameter. The number of molecules in any gas may be calculated from the well-known Avogadro number, which states that, at standard conditions 22.4 liters of a gas contain 6.06×10^{23} molecules or 2.7×10^{22} molecules per liter.

GAS LAWS AND THE KINETIC THEORY

Boyle's Law.—Many years before the kinetic theory of gases was postulated, certain regularities in the behavior of gases were noted. These were eventually formulated into the gas laws. The oldest of these is Boyle's law, which states that, at constant temperature, the pressure exerted by a gas is inversely proportional to the volume it occupies, or that the pressure multiplied by the volume of the gas is a constant. This may be expressed mathematically by

$$P \sim \frac{1}{V} \qquad \text{or} \qquad PV = k$$

The question may be asked, how may this law be correlated with the kinetic theory? The first point to be settled is to explain pressure on the basis of the kinetic theory. Since most gases are kept in containers, the molecules of the gas, in addition to colliding with each other, collide with the walls of the vessel. In fact, the walls of the vessel are subjected to a continual bombardment of molecules, very much like hailstones striking a roof. This gives rise to a pressure on the walls of the container. The greater the number of molecules striking the wall the greater is the pressure exerted on the wall. It is obvious that if the same number of molecules occupied half the volume, there would be twice as many collisions with the walls and conse-

quently the pressure would be twice as great. For example, 4 grams of helium occupy a volume of 22.4 liters at 0°C. and 1 atm. pressure, but if the volume is changed to 11.2 liters, then the pressure becomes 2 atm. However, the product of the pressure and the volume remains constant at 22.4 liter-atm. If the volume were reduced to one-quarter of the original volume (5.6 liters), then the pressure would be four times as great (4 atm.), and the pressure-volume factor would still be constant. This is a simple explanation of the law that was first enunciated by Robert Boyle in 1662 as a result of his researches.

Charles's Law.—The next gas law to be considered is Charles's law, which states that the volume occupied by a gas at constant pressure is directly proportional to its absolute temperature, or, stated mathematically

$$V \sim T \qquad \text{or} \qquad \frac{V}{T} = k$$

Since, from Boyle's law, we know that $P \sim 1/V$, hence P and V are interchangeable, and we may write $P \sim T$. This means that the pressure depends upon some quantity called the temperature. What is the meaning of temperature when the term is applied to groups of molecules? Or, to phrase this question differently, what conditions other than change in volume will cause an increase in the number of collisions with the walls? If a greater velocity is imparted to the molecules, they will strike the walls more frequently and consequently cause an increase in pressure. This, ultimately, is the meaning of temperature as applied to gases. When a gas is heated, the molecules move more rapidly, and as a result, there is an increase in the pressure if the gas volume is kept constant, or, if the pressure is kept constant, the volume increases.

Dalton's Law.—This brings us to Dalton's law of partial pressures, which states that, in a mixture of gases that do not react with each other, each gas exerts its pressure independently of the other gases, as if it alone were filling the vessel. In a mixture of two gases A and B in a vessel, the total pressure exerted is equal to the total number of collisions with the walls. The pressure exerted by gas A will be due to the collisions of molecules of A with the walls, regardless of the presence of gas B. If the molecules of A undergo one million collisions with the wall in a given unit of time, the total pressure exerted by A will be the pressure due to the million collisions. If molecules of gas B are introduced and if B does not react with A, the total number of collisions will increase, causing an increase in the total pressure. However, the

pressure exerted by A remains the same, whereas the total pressure exerted is the sum of the pressure of A plus the pressure of B.

The Combined Gas Laws.—For practical purposes, it is often advantageous to use the combined form of the Charles's and Boyle's law. This is customarily formulated as

$$PV = nRT$$

where P = pressure
V = volume
T = absolute temperature
R = universal gas constant for 1 mole
n = number of moles of gas

Experimental Verification of the Gas Laws.—The gas laws are expressions of experimental facts. However, the practical evidence upon which they were based has been found to be not quite so exact as the laws would have us believe. For instance, according to Charles's law, gases at constant pressure should expand $\frac{1}{273}$ of their volume for each degree rise in temperature. Careful experiments have shown that all gases do not exhibit this same rate of expansion. Table XIV lists the rates of expansion of several gases with increasing temperature at constant pressure.

TABLE XIV.—RATE OF EXPANSION OF GASES PER DEGREE RISE IN TEMPERATURE AT CONSTANT PRESSURE

Air	1/272.8	Oxygen	1/272.2
Hydrogen	1/273	Helium	1/273
Nitrogen	1/272.6	Carbon dioxide	1/270.4

From this evidence, we can deduce that Boyle's and Charles's laws are rigidly applicable only over limited ranges of temperature, pressure, and volume.

Ideal Gas.—An ideal gas is one that, at constant temperature, in strict observance of Boyle's law, has the same PV value regardless of variations in either the pressure or the volume. However, all known gases show variations in their behavior as compared to that of an ideal gas. For example, hydrogen and helium, at 0°C., show a progressive increase in their PV values as either the pressure or the volume is increased or decreased. Oxygen and nitrogen, on the other hand, show a decrease in the value of PV with changes in either pressure or volume until a certain minimum is reached, at which time the pressure-volume product starts to rise. These deviations are slight and tend to disappear as the pressure of the gas approaches zero. It is common practice to study the behavior of actual gases in terms of their deviation from the behavior of ideal gases.

Nonideality of Gases and van der Waals' Equation.—Two of the factors responsible for the nonideality of gases are (1) that molecules of a gas, contrary to the kinetic theory, do exert an attractive influence upon each other, especially at higher pressures, and (2) that whereas ideal gas molecules would merely be points in space, the molecules of an actual gas occupy a definite volume.

It is clear that the attractive influence among molecules is negligible at low pressures because of the large amount of free space between them. At high pressures, however, the gas molecules approach one another, and the attractive influence is therefore more apparent. This force, whose magnitude varies inversely as the square of the total volume, tends to decrease the total volume of the gas. If this attractive influence, at a volume of 1 liter, is symbolized by the letter a, then a/V^2 will express the attraction at any other volume. Since this attractive influence tends to decrease the volume occupied by the gas, it acts in conjunction with the externally applied pressure and must be added to this pressure. The total pressure of the gas is therefore $(P + a/V^2)$.

At low pressures, the volume occupied by the molecules of a gas is negligible when compared with the total volume of the gas. Therefore, the free space and the total volume are essentially identical. For example, if the pressure exerted on a gas is doubled, the resulting volume occupied by the gas would be one-half of the original volume. The volume occupied by the molecules is still negligible. The gas, then, obeys the simple Boyle's law. However, let us assume that the gas is under high pressure and that the volume occupied by the molecules is equal to $\frac{1}{20}$ of the total volume. The volume of free space is then 20 − 1, or 19. If this gas is further compressed to one-half its present volume, the volume of free space is now 10 − 1, or 9, and the pressure is $\frac{19}{9}$ instead of 2, as would be expected from Boyle's law. This law must therefore be amended so that the volume expression takes into account the free space or true volume of the gas. The free space is equal to the volume of the gas minus the volume occupied by the molecules. This may be expressed mathematically as $V - b$, where b is the effective volume of the molecules. With this correction, Boyle's law now becomes $P(V - b) = k$.

The simple gas law equation may now be written as $(P + a/V^2)(V - b) = k$. This is van der Waals' equation. In actual practice, it has been found that at ordinary pressures (1 to 2 atm.), the actual deviation of gases from Boyle's law is within the limits of experimental error. The widest deviation occurs for most gases in the ranges of 50 to 100 atm.

It is apparent then that the simple form of Boyle's law, $PV = k$, may be used for ordinary work. The gases that deviate most widely from the simple law are those that are most easily liquefied, since in these cases, the intermolecular attractive influence is strongest. Nitrogen, for example, which is liquefied with difficulty, departs less from Boyle's law than does carbon dioxide, which is liquefied much more readily.

It should be noted that the two factors, attractive influence and molecular volume, which cause substances to deviate from the gas laws, act in opposite directions, the former decreasing the value of PV, the latter increasing the value of PV. There should be, therefore, for each gas a pressure at which these effects balance each other and the simpler law holds true.

SOLIDS

In sharp contrast to the general shapelessness of gases and the chaotic movements of the molecules comprising them, solids are characterized by a definite shape and form. The units comprising a solid substance are rigidly held together by forces of attraction that are considerably greater than those present in gases or liquids. As a result, solids possess considerable mechanical strength and rigidity. Two distinct classes of solid substances are known. The first class consists of substances that are crystalline in character, and the second class consists of the so-called amorphous or shapeless solids.

Crystals.—Crystalline material is characterized by a regularity of shape and a definite arrangement of the component particles. The crystals arise by growth, either from an evaporating solution or from a freezing liquid. During this process, there is a systematic growth from the unseen molecular particles to the point at which the outlines of the crystal are macroscopically evident. The visible crystal has the same form as at the very moment of genesis, and the completed crystal is merely an external manifestation of a specific and characteristic internal structure. We are familiar with the lacy, fernlike structure of ice or snow crystals on a windowpane. This is similar to viewing a very thin section of a crystal and is indicative of the general appearance of thin crystalline layers. Larger crystals, obtained from solutions, show definite three-dimensional outlines.

Amorphous Substances.—Among the amorphous substances, glass is a typical example. It does not exhibit any definite shape or form, and substances of this type are considered to be liquids in a very viscous state. There is, however, some ground for the belief that certain amorphous substances are in reality microcrystalline powders

whose crystalline nature can only be determined by means of X-ray spectroscopy. The particles comprising amorphous substances are generally in a far less ordered arrangement than in crystals. They do, in fact, bear a closer resemblance to liquids than to crystalline solids.

Crystal Structure.—Since each crystal has a definite structure, the forces between contiguous particles are exerted in a definite direction. This definiteness of structure implies that each particle has a fixed position of equilibrium but does not preclude the conception that it is still free to move about in highly restricted areas and with a slight randomness of motion. We may assume that in the equilibrium state, the particles perform oscillations of very small magnitude about their fixed points of equilibrium. The application of heat will obviously increase the amplitude of these oscillations. At a certain temperature, these oscillations may become so great that the particles begin to collide with each other and may break loose from their fixed points of equilibrium. When this temperature is reached, the solid structure disappears, and melting, or liquefaction, takes place. This temperature is the fusion or melting point. Since the particles comprising a solid exert considerable attractive force on each other, a certain amount of work must be done in separating the particles. The amount of work done, expressed as heat energy, is called the heat of fusion. This is defined as the number of calories required to convert completely 1 gram of a solid at its melting point to the liquid state, or vice versa. There are also other forces acting between particles in the solid state. These are the forces of repulsion that act to make solids only slightly compressible. The forces of repulsion increase much more rapidly than do the forces of attraction when pressure is applied to a solid, and therefore the distances between solid particles are only slightly reduced. Under ordinary conditions in a solid, the two sets of forces are in equilibrium.

X Rays.—Our primary interest in solids is not with the outward appearance of crystals but is rather centered on the internal arrangement of the particles making up the crystal. All crystalline substances may be fractured or split along definite planes of cleavage. The splitting of sheets of mica into extremely thin plates is a good example of this phenomenon. This indicates, of course, that each individual crystal has its component particles arranged in a very definite and characteristic structural pattern. The elucidation of the internal structure and arrangement of crystalline substances has been made possible by the use of X rays, which are light waves of extremely short wave length. The wave length of X rays is of the order of 10^{-8} cm., as contrasted with 10^{-5} cm. for visible light and 10^{5} meters for radio

waves. It has been shown that the distance between contiguous particles in crystalline substances is approximately of the same order of magnitude as the wave length of X rays; *i.e.*, the particles are separated from each other by distances of the order of 10^{-8} cm.

The reasoning that led to these conclusions was based upon well-known facts obtained during experiments with so-called monochromatic light. When light falls upon an object whose size is of the same order of magnitude as the wave length of the light, a perfect shadow is

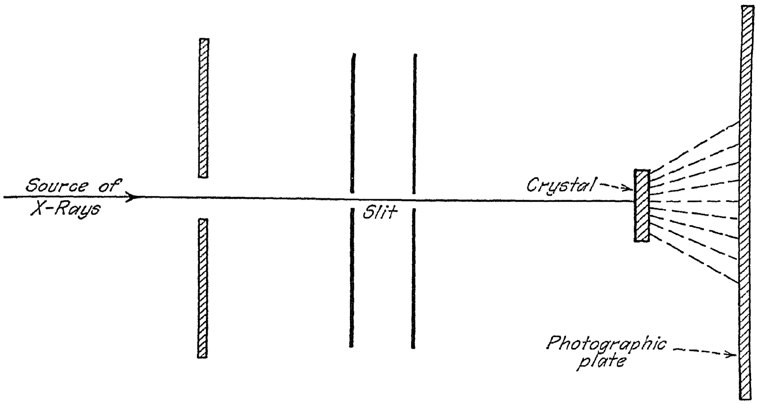


FIG. 27.—Diagrammatic sketch of the apparatus used to take X-ray pictures of crystals.

not cast, but the light is diffracted or scattered. This phenomenon can be investigated by means of a diffraction grating. This grating consists of metal or some other material upon which a large number of very fine lines have been ruled. When monochromatic light is allowed to fall upon such a grating, the fine lines act as obstacles in the path of the light, causing it to be diffracted and giving rise to a number of images.

In a crystal, the orderly arrangement of the particles is the space or crystal lattice. Since the spacing of particles in crystals is approximately 10^{-8} cm., the same order of magnitude as the wave length of X rays, the crystal may be used as a three-dimensional diffraction grating. Laue reasoned that the fundamental effect would be the same and proved it mathematically. If a thin beam of X rays was directed through a thin section of a crystal, the rays would emerge as a number of diffracted beams. If, now, the emitting rays were permitted to strike a photographic plate placed behind the crystal, the plate would exhibit a central spot because of the primary beam and a series of symmetrically spaced dots due to diffraction of the X rays

from the individual particles. Therefore, Laue concluded that the positions of the particles comprising the crystal could be deduced from a consideration of the position of the dots.

These speculations were experimentally verified by Friedrich and Knipping a year later, with the use of the apparatus outlined in Fig. 27. These investigators obtained photographic plates wherein the structural differences of the crystals were demonstrated by a wide variety of geometrical patterns, as illustrated in Fig. 28. Since the Laue dia-

FIG. 28.—Laue photograph of sodium chloride.

grams were difficult to analyze, several later investigators introduced variations in the methods of obtaining the photographic plates with a consequent ease of analysis of the figures obtained. The Braggs suggested that instead of using the crystal as a transmission grating, it might be used as a reflection grating. In order to eliminate the necessity of using large, perfect crystals that were difficult to obtain, a method was developed independently by Hull, and Debye and Scherrer, wherein a thin film of powder composed of fine crystalline particles was used in place of a single large crystal.

The Space Geometry of Crystals.—There are a large number of patterns that may be formed by the arrangement of solid particles in space. By far the most common arrangement found in both elements and compounds is the cubic structure, or lattice, which is the most symmetrical of all arrangements. In this simple geometrical form,

there are three ways in which the particles may align themselves in space (see Fig. 29).

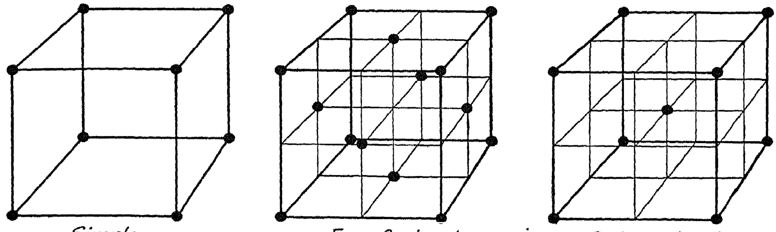


FIG. 29.—Simpler lattice types.

The first is the simple cubic lattice wherein the particles are placed at the eight corners of the cube. The second is the face-centered cubic lattice, differing from the first in that there are also particles centered in each of the six faces. In the third, or cube-centered lattice, there is also a particle in the center of the cube. Substances like KCl, AgCl, NH_4I, and MgO are examples of the simple cubic type. Most of the metals are of the face-centered or cube-centered lattices. The face-centered is exemplified by Al, Cu, Ag, Au, and Pt. The last type is illustrated by Na, K, Cr, Fe, and W.

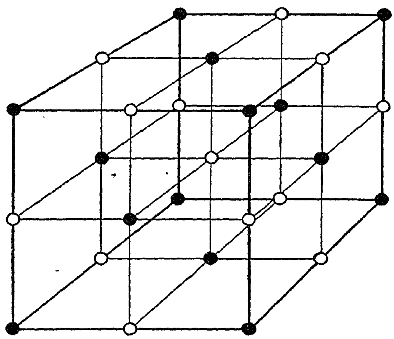


FIG. 30.—The crystal lattice (cubic) of the sodium chloride crystal.

Structure of Sodium Chloride. In considering the use of X rays in the determination of crystal structure, let us use as an example sodium chloride, which exhibits a cubic lattice. This substance, like rock salt, was, in fact, used by the Braggs in their studies. Theoretically, the crystal lattice of this compound either could consist of sodium chloride molecules as the unit particles or have the components of the molecule (Na and Cl) separated. If the latter were true, the lattice would then consist of sodium atoms or ions combined with a lattice of chloride atoms or ions. From the evidence obtained with X-ray methods, we can say that there are in sodium chloride two separate lattices. One of these contains only sodium ions (Na^+); the other contains chloride ions (Cl^-). Referring to Fig. 30, we see that each sodi-

um ion is surrounded by or shared by six chloride ions and that each chloride ion is surrounded by or shared by six sodium ions. The identity of the molecule in crystals of this type has disappeared, and each of the ions belongs equally to the six ions of opposite charge that surround it. The term molecule, then, must be applied to the whole crystal and not to a single unit of the crystal. In a great many cases, of course, certain crystals do have groups of atoms as the unit particles of their crystal lattices. In these cases, the groups of atoms are held together by primary or secondary valence forces.

Isomorphism.—In the late eighteenth century, the Abbé Haüy, recognized generally as the father of crystallography, postulated that crystals that were identical in form must be identical in chemical composition and, conversely, that a difference in chemical composition implied a difference in crystal form. Shortly thereafter, many exceptions were noted to this axiom. The work of Mitscherlich, from 1818 to 1820, contributed to disproving these postulates. While investigating the crystalline forms of various phosphates and arsenates, he noted that compounds of similar composition, containing the same number of atoms, had almost exactly the same crystalline form. In putting forward what is now known as the **law of isomorphism,** Mitscherlich stated his belief that the phenomenon was due to the ability of chemically similar but different compounds to exist in the same crystalline form. Originally, he considered that the same number of atoms combined in the same way to produce the same crystalline structure regardless of the chemical nature of the atoms. In other words, the shape of the crystal was determined by the number of atoms and their manner of combination. As a result of later investigations, Mitscherlich's statements were somewhat revised. The generalization now accepted states that substances that have similar chemical composition very often have similar crystalline forms. Also, one atom of a crystal may be replaced by another atom without a change in crystalline form if the two elements are chemically similar. The alums are excellent examples of isomorphism. Common alum, $KAl(SO_4)_2 \cdot 12H_2O$, and chrome alum, $KCr(SO_4)_2 \cdot 12H_2O$, are definitely isomorphous. Other well-known examples are Epsom salts, $MgSO_4 \cdot 7H_2O$, and zinc sulfate heptahydrate, $ZnSO_4 \cdot 7H_2O$. There are, however, a number of exceptions to this rule. The law of isomorphism does not give a true insight into the conditions necessary for isomorphism. A number of salts have similar chemical composition but are not isomorphous ($NaCl$ and KCl; KF and KBr). On the other hand, there are compounds like $NaCl$ and $AgCl$ that bear only a slight chemical resemblance to each other but that are isomorphous. Finally,

it has been found that isomorphism may occur even among substances that differ widely in chemical behavior ($BaSO_4$ and $KMnO_4$).

Obviously, then, complete identity of crystal structure is not a rigid criterion of isomorphism. One of the true criteria of isomorphism is the ability of substances to form mixed crystals. If two substances are truly isomorphous, they will both crystallize from solution together, the crystals always containing varying proportions of each substance. For example, $CuSO_4$ and $FeSO_4$ are isomorphous. When a solution containing these two substances is allowed to crystallize, the copper sulfate is always found to contain some ferrous sulfate, and regardless of the number of times the former is recrystallized, there is always some contaminant present. Fractional crystallization is obviously not sufficient to purify the copper sulfate. However, if the iron is oxidized with nitric acid to the ferric condition, the crystals are no longer isomorphous, and they can be separated. The sulfates of zinc and magnesium also defy separation by fractional crystallization.

The study of the crystalline form and the properties of crystals is now made microscopically, this branch of analytical science being known as chemical microscopy. Those crystals whose physical properties are the same in all directions are called isotropic, whereas those whose physical properties depend upon the angle in which the measurement is made are called anisotropic.

LIQUIDS

Our discussion of gases and solids has provided us with an insight into the behavior and structure of the two extremes in states of aggregation. Liquids occupy a position intermediate between these two forms, and we might expect that they would resemble one or the other to some extent. As we shall see, liquids are fundamentally similar to gases both in behavior and structure. There must be, of course, some distinguishing characteristics between the liquid and gaseous states. We have already seen that gases are characterized by their ability to expand and fill the containers in which they are confined and that they possess, in addition, low density and viscosity. Liquids, on the other hand, have a definite volume for a given mass but have no definite shape. They have a greater density and viscosity than gases, and they possess a much lower degree of compressibility. In part, these differences may be explained by the fact that in gases the kinetic energy is much larger than the forces of attraction between the molecules, whereas in liquids the attractive influence is the greater. These variations, however, are not fundamental in character but are differences in degree only. The chief reason for the demarcation between

the gaseous and liquid states of aggregation is probably due to the difference in the magnitude of the intermolecular forces of attraction and repulsion in the two states. These variations are governed chiefly by pressure and temperature relations, which may be so adjusted that the apparently striking differences are eliminated.

We may assume that the unit particles of liquids are molecules (see Chap. VI). Obviously, the distance between contiguous particles is much less than in the gaseous state, and the free path between the molecules is very minute. Because of the closeness of the particles to each other, the forces of attraction exerted upon them are considerably greater than in the case of gases. This accounts for the slight compressibility of liquids.

That liquids represent a highly condensed form of matter may be illustrated by the following example. When 1 ml. of water at its boiling point is converted to vapor at the same temperature, the volume occupied is about 1,700 ml. Since energy in the form of heat was required to bring about the change, we may safely assume that liquids possess less energy than gases. The heat required to bring about this change is called the heat of vaporization.

READING REFERENCES

FINDLAY, A.: "The Spirit of Chemistry," Chaps. VI and VII, Longmans, Green and Company, New York, 1930.

GETMAN, F. H., and F. DANIELS: "Outlines of Theoretical Chemistry," 6th ed., Chaps. II, III, and IV, John Wiley & Sons, Inc., New York, 1937.

MACDOUGALL, F. H.: "Physical Chemistry," Chaps. III, IV, and V, The Macmillan Company, New York, 1936.

MELDRUM, W. B., and F. T. GUCKER: "Introduction to Theoretical Chemistry," Chap. II, American Book Company, New York, 1936.

QUESTIONS

1. If 275 ml. of hydrogen is collected over water at 27°C. and 752 mm. pressure, what will be the volume of dry gas at standard conditions?

2. If 150 ml. of oxygen is collected over water at 22°C. and 765 mm. pressure, what will be the volume of dry gas if collected over mercury at 35°C. and 740 mm. pressure?

3. Compute the volume of SO_2, collected at 25°C. and 770 mm. barometric pressure, produced by the interaction of 5 g. of copper and concentrated H_2SO_4.

4. In terms of the kinetic theory, distinguish the properties that serve to differentiate solids, liquids, and gases.

5. A definite volume of nitrogen exerts a pressure of 0.25 atm. Three times as much oxygen is introduced into the vessel. What is the pressure of the mixed gas? If a volume of chlorine, equal to two and one-half times the original volume of nitrogen, is added to the mixture, what is the total pressure?

6. A gas occupies a volume of 50 ml. at 16°C. and 750 mm. pressure. At what temperature will the volume become 30 ml. if the pressure remains constant?

7. In terms of the kinetic theory, account for each of the following:

a. Crystalline form of substances
b. Melting of crystalline substances
c. Vapor pressure of a liquid
d. Freezing point of a liquid

8. Five hundred milliliters of a gas at S.T.P. was heated until the volume increased to 750 ml. and the pressure became 775 mm. Calculate the temperature.

9. Why do gases not obey Boyle's Law at high pressures? Why does Charles's law not hold rigidly at elevated temperatures?

10. How many molecules are there in a liter vessel that has been evacuated to 0.2 mm. at 0°C.?

11. Describe briefly the methods used to determine crystal structure. Draw the crystal lattice of KBr.

12. Given that 1 mole of a gas occupies 22.4 l. at 0°C. and 1 atm. pressure, calculate what the volume would be at 600°C. and 300 atm. pressure. Use both the simple gas equation and van der Waals' equation. Calculate, also, the deviation of the values derived from the simple gas equation from those derived from van der Waals' equation.

VAN DER WAALS' COEFFICIENTS

Gas	a $\frac{\text{atm.} \times (\text{liters})^2}{(\text{moles})^2}$	b $\frac{\text{liters}}{\text{mole}}$
CO_2	3.592	0.04267
Cl_2	6.493	0.05622
He	0.03412	0.0237
O_2	1.360	0.03183

CHAPTER VI

REACTIONS OF CHEMICAL COMPOUNDS

I. PURE SUBSTANCES

The most puzzling questions the student of chemistry asks himself are: Why do reactions occur? What is a chemical reaction or change? Why do substances sometimes react to form one compound, sometimes another, often a mixture of products and very often do not react at all? When is a substance a chemical compound, and when is it simply a mixture? These questions cannot be answered very simply. Some of them may be answered by definitions. These definitions are usually meaningless, however, if they are too narrow and futile if they are too broad. Also, the answers to these questions vary with the year in which they are asked. One of the major tasks of theoretical chemistry is an attempt to formulate an intelligible answer to these questions.

The earliest answers were anthropomorphic, *i.e.*, an element, A, "liked" another element, B, more than it "liked" a second, C; hence it combined with the first in preference to the second, C; or, to put it more scientifically, element A had greater affinity for element B than for C. This is not really an explanation but, rather, an observation; it does not tell us why the element A "likes" the element B more than C. In a sense, most of the explanations of reactions offered state the same thing. We are, however, gradually arriving at concepts that are providing a more fundamental answer to these questions. Whether we shall ever be able to answer this question "why?" is problematical, since it eventually resolves itself into a question of philosophy. Nevertheless, we shall attempt in this section to give as fundamental an answer as scientists have been able to wrest from nature.

THE KINETIC APPROACH

Let us consider two atoms moving about in a space of 1 cc. The likelihood of these two atoms colliding is remote, and since reaction is always preceded by collision, the likelihood of reaction occurring is more remote. But this is an improbable case, since the likelihood of such empty space occurring on the earth is extremely remote. It may occur in interstellar space, though not upon the earth. Let us, therefore, consider a much more crowded space, such as occurs on earth

where atoms do collide and collide very frequently. In such a space, let us consider two molecules that are approaching each other at such velocities and in such a direction that a collision will occur. The question is, will these two molecules react? By a collision we do not mean that the nuclei actually collide. It is very doubtful if nuclei collide even in interatomic transformations, such as those caused by the cyclotron. What is meant is that the atoms or molecules approach sufficiently close to each other to enable the intermolecular forces to come into play. After the collision, the molecules either depart on separate paths or react, *i.e.*, travel in a common path (see Fig. 31).

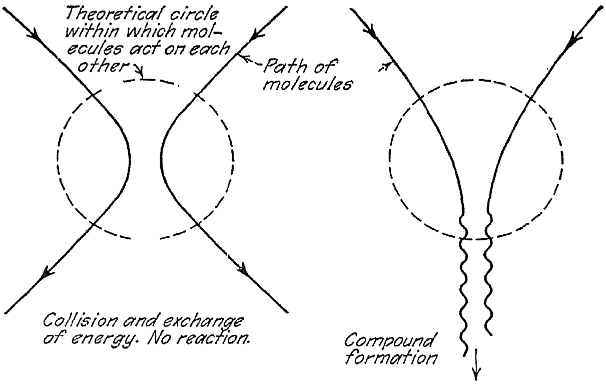


FIG. 31.—Molecular collisions.

The Governing Conditions.—Now, to return to the question as to whether the two molecules will react. This question really does not mean much, since any two molecules or atoms will react, given the right conditions. The question, then, should really be, what conditions determine whether two atoms undergoing a collision will react? There are several factors, not necessarily independent, that determine whether reaction will take place. These are:

1. How strong are the forces of attraction and repulsion between the atoms?

2. What is the energy content of each molecule (*e.g.*, velocity, among other things)?

3. How is the energy distributed in the molecule at the instant of collision; and as a corollary, what is the angle of approach between the molecules?

To illustrate these points, we may select a very homely example. Assume that two boys are running down the street and wish to grasp

each other's hands. If they are approaching each other from opposite directions, their speed must be slow enough so that their momentum will not break their handclasp. If their speed is too great, they will clasp hands momentarily, but the momentum that their bodies have acquired will break the handclasp. The force of joining will, however, cause them to swerve. The greater their momentum the less will be the diversion caused by the momentary handclasp. If the boys are running in the same direction, one a little faster than the other, they could readily clasp hands as they came together. The handclasp would force one of the boys to run a little faster and the other to run a little more slowly, the exact deviations depending upon their respective weights (mass). If, on the other hand, the boys were running in the same direction but at greatly different speeds and tried, as they passed each other, to clasp hands, the handclasp might not be strong enough; hence all that it would do would be to jerk the boys into another direction, slowing the fast one while speeding up the slow one. We think of atoms and molecules as behaving in a way similar to these boys. In a similar way the subject of thermal decomposition may be examined. If, when two atoms joined by a bond collide with another atom, the energy of collision is great enough, the molecule may break up, *i.e.*, dissociate.

Let us now examine the third factor, the distribution of energy in the molecule at the moment of collision and the angle of approach of the molecules. Returning to our example of the two boys, if each boy held in one of his hands a bag of books, it is evident that the boys could clasp hands only if, in addition to the conditions of speed, they approached each other in certain directions. This illustration applies to molecules when different parts of the molecules are more reactive than others. In considering the distribution of energy in the molecule, let us take the following example: If each of the two boys running down the street is juggling a ball, *i.e.*, throwing it from hand to hand rhythmically, will they be able to clasp hands as they pass each other? This will, of course, depend upon which hand the ball is in at that moment, *i.e.*, whether their ball juggling is in phase. In many molecules, the attraction at a given point in the molecule may vary periodically because of the oscillation of the electrons or even because of the oscillation of a light atom. The probability, therefore, of a collision resulting in compound formation will depend upon whether the colliding molecules are in phase. If one examines these requirements for reaction, one can see that, if a few billion collisions occur each second, it is highly probable that in at least some of these collisions, the conditions will be just right, and reaction will occur. We may, therefore, state that if two sub-

stances are mixed, all possible reactions between them will occur to some extent.

The Extent of a Reaction.—The next question is, to what extent will each possible reaction occur? This is a very important question, since we know as a general rule that if we mix two particular substances under certain specific conditions, only very definite reactions will occur. The answer seems to be one of statistics; if we have several billion molecules having a particular energy distribution and undergoing a certain number of collisions each second, which reaction or reactions of these substances will predominate?

First we must realize that, to judge by common criteria, quite a number of molecules must react before we are aware of the fact. For instance, there are approximately 2.7×10^{19} molecules per ml., *i.e.*

$$27{,}000{,}000{,}000{,}000{,}000{,}000 \text{ molecules/ml.}$$

One of our most sensitive tests, the formation of lead sulfide from lead ion and sulfide ion, is barely visible if the concentration of lead ion is 0.000025 per cent. This means that there must be at least 4.25×10^{12} (or 4,250,000,000,000 ions per ml.) ions of lead present before the reaction becomes visible. If the concentration is less, we shall not know whether the reaction has occurred. Hence a reaction may occur to such a slight extent that it will not be visible.

THE ENERGY APPROACH

The First Law.—In addition to the statistical approach outlined above, the problem has also been approached from another angle. In this attack, there are several axioms. The first is the familiar statement that the energy in an isolated system is always constant, *i.e.*, *energy can be neither created nor destroyed.* From this statement, knowing that energy can exist in many forms, we may say that in any system the

$$\begin{aligned}\text{Total energy} = {} & \text{work energy} + \text{heat energy} + \text{chemical energy} \\ & + \text{gravitational energy} + \text{electrical energy} + \cdots\end{aligned}$$

In this system, one form of energy may be transformed into another form without changing the total energy. Now, each type of energy is composed of the product of two factors, the *capacity factor* and the *intensity factor*. Let us consider what this means. If we have two blocks of wood, one of which has a mass of 1 lb. and the other a mass of 2 lb., and if they are held 1 ft. above the ground, the amount of potential energy that each block possesses, *i.e.*, the amount of work that it would do if allowed to fall to earth, would, in the case of the body

weighing 1 lb., be 1 ft.-lb. and, in the case of the 2-lb. body, be 2 ft.-lb. The mass is the capacity factor, and the height through which it can fall is the intensity factor. In this example, the intensities are equal, but the energies are different, because the capacities are different. Let us take another example. We have a lake with a dam at one end, so that the water behind the dam is at a higher level than the water in the lake (see Fig. 32). Only the water behind the dam and above the level of the lake has the ability to do work; *i.e.*, it possesses potential energy. If the dam is opened, the level of the water in the dam will fall to the level of the lake. The amount of water behind the dam and above the level of the lake is the capacity factor; the height is the

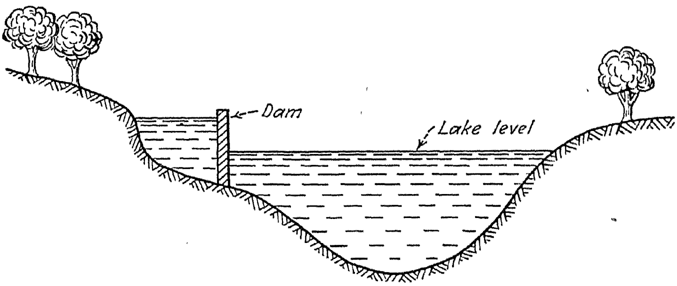


FIG. 32.—Potential energy stored behind a dam.

intensity factor. If we examine this illustration, we see that the intensity of any given little portion of the water above lake level depends upon its height and, therefore, that the intensity varies with the height. When the dam has been opened and the total work accomplished, the capacity, *i.e.*, the amount of water at lake level, has been increased and is equal to the total amount of water. The intensity, however, is now equal throughout, and this system can do no more work.

The Second Law.—This brings us to the second axiom or law, which states that all systems tend to reach equilibrium. If, in our last example, there were several dams surrounding the lake and the water stood at different levels behind each one, then, if we opened all the dams, the water level would become equal throughout. Thus we see that the system would have reached equilibrium.

Types of Energy.—Let us now consider what the components are of the various types of energy previously discussed. The first is **work energy.** The intensity factor of work energy is the pressure, and the capacity factor is the volume. From the discussion of gases in Chap. V, it may be seen that the amount of gas is the volume. In doing

work, this volume of gas must act against a certain pressure. Hence the intensity factor is the pressure and the capacity factor, the volume of the gas. In considering work energy in relation to solids and liquids, we define the intensity and capacity units in a different manner, more suitable for those states of aggregation.

The intensity factor for **thermal energy** (the next form of energy) is the temperature, and the capacity factor is the entropy, the quantity of heat. The capacity factor for **chemical energy** is the mass, and the intensity factor is the chemical potential. These three types of energy are those that are usually considered in chemical reactions. It is not necessary at this point to go into a more detailed development of these methods of analysis. Suffice it to say that by the use of such methods, it is possible to obtain a quantity called, variously, the free energy or the **Gibbs free energy.** If, in a given reaction, we subtract the free-energy content of the products from the free-energy content of the reactants, we obtain another quantity called the change in free energy. The algebraic sign of this quantity tells us whether the reaction *can* proceed, but it does not tell us if it *will* proceed at a measurable rate. The change in free energy is essentially the difference between the chemical energy of the products and the chemical energy of the reactants. The extent to which any possible reaction will occur is then dependent upon the sign and the magnitude of this quantity.

Correlation of Kinetic and Energy Aspects.—This energy concept of reaction and the collision concept previously discussed actually supplement one another, as may be seen from the following example. The sign of the numerical value (which we can calculate) of the change in free energy tells us that, if we mix hydrogen gas with oxygen gas, they can react to form water, but it does not tell us how long it will take. We know that it will take a very long time, since mixtures of hydrogen and oxygen are quite stable ordinarily. This can be explained from a molecular viewpoint. In the hydrogen molecule, there are two atoms, as in the oxygen molecule, and it seems that before the hydrogen and oxygen can react, we must have single atoms. However, the kinetic energy of the molecules in the mixture, at ordinary temperatures, is such that the occurrence of single atoms is relatively rare, and consequently the likelihood of collision between individual atoms is very remote. Accordingly, the reaction will not take place at ordinary temperatures. If, however, we heat the mixture, the number of collisions and the energy of each collision increase, and therefore there are more single atoms and more collisions between single atoms. Since each such collision releases energy, the kinetic energy increases, and the whole material reacts rapidly.

THE CHEMICAL BOND

Primary Valence Bonds

We have been discussing at great length the conditions necessary for reactions to occur, but we have said very little concerning the forces that hold the molecules together. We know that, when a reaction occurs, the two reacting atoms travel away on a common path, undergoing a series of vibrations against each other, and in a previous chapter, we learned that several types of bonds exist between atoms. The question now is, what determines the type of bond that is formed, and how does the type of bonding influence the subsequent behavior of the molecule?

This question is not one of the simplest to answer, for although the first result is that the molecules stick together (attract each other), the forces that cause them to attract each other will vary in strength, and this variation will be reflected in the subsequent behavior of the molecule. Let us consider what these forces are and how they affect the behavior of the molecule. First we must remember that these forces are not independent but are only descriptions of extremes. Each of these types of linkage is represented in the "pure form" in some molecules, but other molecules fall into intermediate classes, where the forces acting cannot be classified so distinctly.

The Homopolar Bond.—As a first type of linkage, we shall consider the homopolar bond. Here the two atoms share a pair of electrons, one of which was contributed by each atom. The resulting molecule is more stable than either of the parts. Further, the two participating atoms attract the shared pair equally; *i.e.*, the two electrons of the shared pair travel around both atoms and spend as much time under the influence of one atom as of the other. This describes one extreme case.

The Heteropolar Bond.—At the other extreme is the heteropolar bond, where one atom takes an electron away from another. There the transfered electron revolves solely around the host, and it does not enter the sphere of influence of the other atom at all. As a consequence, one atom is now positively charged, and the other is negative. The force that holds them together is the electrostatic force due to the negativity of one atom and the positivity of the other. This is the other extreme case. At one extreme, the atoms are very particular as to which atom they are attached to; at the other extreme, an atom desires only to be in the neighborhood of an oppositely charged atom, but it will readily trade its partner for another of the same charge.

The Semipolar Bond.—One type of bond that is intermediate between these two extremes is the semipolar bond. In this bond, one atom that has a "lone pair" of electrons (*i.e.*, two electrons that are not shared) will share this pair of electrons with another atom that has space in its electronic superstructure for two more electrons. In this case, the pair of electrons travel in orbits around both atoms. If the atoms are neutral originally, that which donates the electrons becomes a little more positive, and the one accepting the lone pair becomes a little more negative. This is logical, since the first atom, the donor of the lone pair, was neutral when it had all its electrons, but if it shares two of its electrons, it will no longer be sole "owner" of these negative charges and hence becomes a little more positive. Similarly, the acceptor of the lone pair becomes a little more negative. Of course, the molecule, as a whole, still remains neutral. If one of the participating atoms has a charge, the same conditions exist in the molecule as before, but the molecule, as a whole, is electrically charged.

The Valence Forces.—The forces just described are usually called the **primary valence forces** and play the major part in the formation of the atomic aggregates that we call compounds. However, another series of forces exist that also cause atoms to travel in a common path. These forces are called the van der Waals' forces or, more usually, the **secondary valence forces.** They are, in general, much weaker than the primary valence forces and may be divided into three classes, which vary chiefly in their origin and in the strength of the resulting bond.

Secondary Valence Forces

Rigid Dipoles.—Let us assume that we have a neutral molecule having a bond that is intermediate between a heteropolar and a homopolar bond. Because of the effects previously described, the molecule,

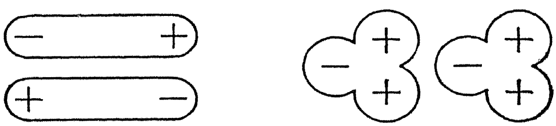


Fig. 33.—Dipole compounds: two types.

although neutral as a whole, will have one part that is more electropositive and another part that is more electronegative than the adjoining sections of the molecule. As a consequence of this fractional charge, if two of these molecules approach one another, they will align themselves in such a way that the negative charge of one molecule is as close to the positive charge of the other molecule (and vice versa) as the geometry of the molecule will permit. Thereafter the two

molecules will travel together until sundered by a collision. Compounds possessing bonds of this type are called **dipole compounds.**

Induced Dipoles.—Another variation of this force exists when a compound possessing a dipole approaches a molecule having no dipole, in which the outer electrons, however, are quite mobile. If the negatively charged portion of the dipole molecule approaches the neutral compound, it will repel the mobile electrons and convert the neutral molecule into a temporary dipole. If the positively charged portion approaches, it will attract the mobile electrons and also form a temporary dipole; *i.e.*, the dipole molecule will induce a charge or dipole in the neutral molecule. The induced dipole and the permanent dipole will now attract each other and so form another type of dipole compound. This type of force is, of course, weaker than that between two permanent dipoles.

Dispersion Forces.—The third type of van der Waals' force is the weakest type and was postulated to explain the fact that rare gases, like argon and neon, at high pressures form liquids and solids. For this phenomenon to occur, some type of attraction must exist between the atoms. The primary valence forces are ruled out, since the rare gases form no stable compounds. We know, also, that these molecules are symmetrical; therefore, no dipoles or induced dipoles can exist; but forces do exist! To explain this, London postulated that when the atoms are very close together, they tend to arrange themselves so that their electronic orbits are in resonance with each other. This third variety of van der Waals' forces is called the dispersion force. This postulation has been subjected to experimental verification and has been found valid.

As a last word to this section, let the reader beware lest he think of these types of bonds as separate entities, remote and distinct. After all, all these bonds are the result of the interaction of two electrical systems, each of which is composed of positive charges and negative-charge clouds of variable density—electrons, if you choose. The result is a net attraction or repulsion. From the magnitude of this effect and from the behavior of the resulting system we then reason backward and classify the types of linkages.

REACTIONS BETWEEN GASES

We have now discussed in a general way why reactions occur, but for many purposes we wish to know not only why they occur but also to what extent they occur. This question can be dealt with, for gases, in a statistical manner.

Equilibrium Constants in Terms of Concentration.—Let us suppose that we have two gases, A and B, in a vessel. We know that they will react to form the compound AB. We know, also, that the compound AB will break up again into A and B. We know, too, that after some

time, the reaction will come to equilibrium; *i.e.*, AB will be formed as fast as it decomposes. When this equilibrium has been established, how much of A, B, and AB will be present in the vessel? The reaction may be represented as

$$A + B \rightleftharpoons AB$$

The equation is written with a double arrow to indicate that there is an equilibrium. The concentration, *i.e.*, the number of gram moles per liter of A may be represented by C_A; the number of gram moles per liter of B, by C_B, and the number of gram moles per liter of AB by C_{AB}. The speed with which A will combine with B is given by the formula

$$\text{Speed}_{A+B} = k_1(C_A \times C_B)$$

That is, the speed of this reaction will be determined by a constant k_1, which takes into account the various factors outlined previously (such as the velocity and energy content of the molecules, the energy distribution in the molecules, and the number of collisions per unit of time) multiplied by the concentration of the two reactants. Similarly, the speed of the other reaction, the decomposition of AB will be given by the formula

$$\text{Speed}_{AB} = k_2(C_{AB})$$

At equilibrium

$$\text{Speed}_{A+B} = \text{speed}_{AB}$$

therefore

$$k_1(C_A \times C_B) = k_2C_{AB}$$

or

$$\frac{C_{AB}}{C_A \times C_B} = \frac{k_1}{k_2}$$

Since k_2 and k_1 are both constants, we may substitute another constant for them

$$\frac{k_1}{k_2} = K = \frac{C_{AB}}{C_A \times C_B}$$

K is the equilibrium constant for the reaction

$$A + B \rightleftharpoons AB$$

One might ask why is the constant taken as being k_1/k_2 rather than k_2/k_1. This is purely conventional; both are correct, but since confusion might arise, K

is so taken that in the reaction A + B $\rightleftharpoons$ AB, the concentration of the substances on the right side of the equation appear as the numerator of the term

$$K = \frac{C_{\text{right side}}}{C_{\text{left side}}}$$

For the reaction AB $\rightleftharpoons$ A + B, the decomposition of AB, the equation is

$$K' = \frac{C_A \times C_B}{C_{AB}} = \frac{1}{K}$$

Example 1.—Let us take the decomposition, in the vapor phase, of phosphorus pentachloride. The reaction is

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

The equilibrium constant is

$$K_c = \frac{C_{PCl_3} \times C_{Cl_2}}{C_{PCl_5}}$$

The subscript c is added to K to indicate that the constant is concerned with molar concentrations. Now we shall calculate K_c for the foregoing reaction. The facts, as obtained by analysis, are that at 250°C. and 1 atm. pressure, the phosphorus pentachloride is 80 per cent dissociated. Therefore, if we started with 1 gram mole of PCl_5, at equilibrium (250°C.), we should have 0.8 gram moles of PCl_3, 0.8 gram moles of Cl_2, and 0.2 gram moles of PCl_5. Now we must calculate the concentration in gram moles per liter. One mole of gas would occupy 22.4 liters at 0°C. or 273°A. and 1 atm. pressure; at 250°C. or 523°A., it would occupy

$$22.4 \times \frac{523}{273} = 42.9 \text{ l., volume of 1 mole at 250°C. and 1 atm. pressure}$$

At equilibrium, we have for every mole with which we started 0.2 mole PCl_5, 0.8 mole Cl_2, and 0.8 mole PCl_3, or 0.2 + 0.8 + 0.8 = 1.8 moles. Therefore, the total volume at equilibrium would be

$$42.9 \times 1.8 = 77.2 \text{ l.}$$

The concentration of Cl_2 is

$$C_{Cl_2} = \frac{0.8}{77.2} = 0.0104 \quad \text{mole/liter}$$

and

$$C_{PCl_3} = \frac{0.8}{77.2} = 0.0104 \quad \text{mole/liter}$$

$$C_{PCl_5} = \frac{0.2}{77.2} = 0.0026 \quad \text{mole/liter}$$

therefore

$$= \frac{C_{PCl_3} \times C_{Cl_2}}{\ldots} = \frac{(0.0104)(0.0104)}{\ldots} =$$

Example 2.—Let us take another typical example, the decomposition of hydrogen iodide gas. Hydrogen iodide at 448°C. decomposes partially into hydrogen and iodine according to the equation

$$2HI \rightleftharpoons H_2 + I_2$$

The equilibrium constant of this reaction is

$$K_c = \frac{C_{H_2} \times C_{I_2}}{(C_{HI})^2}$$

If we start with 2 moles of hydrogen iodide, the volume of the 2 moles at 448°C. will be

$$2 \times 22.4 \times \frac{721}{273} = 118.3 \text{ l.}$$

Since the number of moles is not changed by the reaction, the volume of the mixture will be constant.

After equilibrium has been established, the gram moles of HI remaining will be

$$2 - 2x = \text{moles of HI}$$

and since the gram moles of H_2 equals the gram moles of I_2 and since this is unknown

$$x = \text{g. moles of } H_2$$
$$x = \text{g. moles of } I_2$$

The concentration of the various constituents is now

$$C_{HI} = \frac{2 - 2x}{118.3}$$

$$C_{I_2} = \frac{x}{118.3}$$

$$C_{H_2} = \frac{x}{118.3}$$

and

$$K_c = \frac{C_{H_2} \times C_{I_2}}{(C_{HI})^2} = \frac{\frac{x}{118.3} \cdot \frac{x}{118.3}}{\left(\frac{2 - 2x}{118.3}\right)^2} = \frac{x^2}{(2 - 2x)^2}$$

At 448°C., hydrogen iodide dissociates to the extent of 21.99 per cent;

since x is the amount of dissociation, substituting 0.2199 for x gives

Example 3.—This problem may also be reversed. Let us place in the reaction flask a certain volume of iodine, a, and a certain volume of hydrogen, b; raise the temperature to 448°C., and allow the materials to come to equilibrium. At equilibrium, a certain amount, x, of iodine will have reacted with the same amount, x, of hydrogen. Therefore, the concentration of hydrogen present will be $b - x$, and that of iodine will be $a - x$. The reaction of the x moles of iodine with the x moles of hydrogen will give rise to $2x$ moles of hydrogen iodide. Therefore, for the reaction $I_2 + H_2 \rightleftharpoons 2HI$, we could write

$$K'_c = \frac{C_{HI}^2}{C_{I_2} \times C_{H_2}}$$

but $K'_c = \dfrac{1}{K_c}$ where K_c is the equilibrium constant for this equation written backward. Hence

$$K_c = \frac{C_{I_2} \times C_{H_2}}{C_{HI}^2}$$

And since

$$\begin{aligned} C_{I_2} &= a - x \\ C_{H_2} &= b - x \\ C_{HI} &= 2x \end{aligned}$$

we could substitute these in the equation

$$K_c = \frac{(a - x)(b - x)}{(2x)^2} = \frac{ab - bx - ax -}{4x^2}$$

and solving for x

$$4K_cx^2 = ab - bx - ax + x^2$$

and

$$x^2(1 - 4K_c) - x(a + b) + ab = 0$$

Applying the quadratic formula, we get

$$x - \frac{\pm \sqrt{[-(}}{2(1 - 4K_c)}$$

If the original concentrations were 2 moles of hydrogen to every mole of iodine, $a = 1$ and $b = 2$, and since we know that

$$K_c = 0.01984$$

we can solve the problem

$$x = \frac{\times \qquad - 4(0.01984)]\}}{2[1 - 4(0.01984)]}$$

$$x = \frac{3 \pm \sqrt{9 - 8 + 0.635}}{2 - 0.159} \quad \frac{3 \pm \sqrt{1.635}}{1.841} \quad \frac{3 \pm 1.28}{1.841}$$

$$2.32 \text{ or } 0.934$$

The concentration of HI is

$$C_{HI} = 2x$$
$$C_{HI} = 1.868 \text{ moles}$$

The first answer, 4.64, is manifestly extraneous and is impossible, since the maximum possible yield if the reaction proceeded to completion would be 2 moles of HI, since only 1 mole of iodine was used and 1 mole of iodine can yield no more than 2 moles of HI. Therefore

$$C_{HI} = 1.868 \text{ moles}$$
$$C_{H_2} = b - x = 2 - 0.934 = 1.066 \text{ moles}$$
$$C_{I_2} = a - x = 1 - 0.934 = 0.066 \text{ mole}$$

The last problem may raise the question as to why we both square and double the concentration of the HI. Exactly what is meant by this statement may not be apparent; hence let us choose an example. If we had the following reaction

$$A + B \rightleftharpoons \quad + E$$

the equilibrium constant would be

$$K_c = \frac{\times}{C_A \times C_B}$$

and if we started with 1 mole of A and 1 mole of B, the concentration at equilibrium would be:

$$C_D = x \qquad C_E = x$$
$$C_A = 1 - x, \; C_B = 1 - x$$

and

If now the molecules of D and E were the same, *i.e.*, D and E are identical, the equation would be

$$A + B \rightleftharpoons 2D$$

and

$$K'_c = \frac{C_D{}^2}{C_A \times C_B}$$

Again, if we started with 1 mole of A and 1 mole of B, the concentrations at equilibrium would be

$$C_A = 1 - x,\ C_B = 1 - x$$
$$C_D = 2x$$

Substituting, we should get

$$K'_c = \frac{(2x)^2}{(1-x)(1-x)} = \frac{4x^2}{(1-x)^2}$$

By solving these two equations and equating, we get

$$K_c = \frac{x^2}{(1-x)^2}$$
$$K'_c = \frac{4x^2}{(1-x)^2}$$
$$\frac{K'_c}{4} = \frac{x^2}{(1-x)^2}$$
$$\frac{K'_c}{4} = K_c$$
$$K'_c = 4K_c$$

We see that if the two molecules are alike, the equilibrium constant is four times as great as the equilibrium constant when the two molecules are different. The reason for this will be apparent from the following discussion.

Let us consider four random collisions of the product molecules. When the two molecules are different the collisions would be

D and D	D and E
E and E	E and D

In this case, only the two collisions occurring between D and E will go to form A and B. Let us now consider the other case, where D and E are the same (only D molecules are in the product). The four random collisions would be:

D and D	D and D
D and D	D and D

That is, in the second case, there will be twice as many collisions leading to reaction as in the first; or, to put it differently, if the molecules are alike, the effective concentration is twice as great. Therefore, we can write the equilibrium constant of this reaction as

$$K'_c = \frac{C_D \cdot C_D}{C_A \cdot C_B}$$

and since the effective concentration of C_D is $2x$

$$K'_c = \frac{(2x)(2x)}{(1 - x)(1 - x)} = \frac{4x^2}{(1 - x)^2}$$

Equilibrium Constants in Terms of Pressure.—In most gases, the simple gas law holds

$$PV = nRT \qquad \text{or} \qquad P = \frac{n}{V} RT$$

Now n/V (the number of moles per unit volume) is the definition of concentration; hence, we may write

$$P = CRT \qquad \text{or} \qquad \frac{P}{RT} = C$$

Therefore, in any equation involving gas concentrations, P/RT can be substituted for C. Let us see what would happen if we did this in our first example:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$K_c = \frac{C_{PCl_3} \times C_{Cl_2}}{C_{PCl_5}}$$

Now

$$C_{PCl_3} = \frac{p_{PCl_3}}{RT}$$

$$C_{PCl_5} = \frac{p_{PCl_5}}{RT}$$

$$C_{Cl_2} = \frac{p_{Cl_2}}{RT}$$

where p_{PCl_3} is the partial pressure of PCl_3, etc.

$$K_c = \frac{\dfrac{p_{PCl_3}}{RT} \times \dfrac{p_{Cl_2}}{RT}}{\dfrac{p_{PCl_5}}{RT}}$$

or

$$K_c = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} \times \frac{\dfrac{1}{(RT)^2}}{\dfrac{1}{RT}}$$

$$K_c = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} \times \frac{1}{RT}$$

We can readily see from this relationship that

$$\frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

is a relationship quite analogous to

$$\frac{C_{PCl_3} \times C_{Cl_2}}{C_{PCl_5}}$$

Therefore, it is quite logical to call this K_p or

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = K_c(RT)$$

There is always a relationship between K_c and K_p, but this relationship is determined by the reaction and must be derived for each case. The exact form of the relationship can be obtained by substituting

$$p = CRT \quad \text{or} \quad C = \frac{p}{RT}$$

in the equilibrium equation.

Example 4.—Let us now do a problem involving K_p.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

If we start with 1 mole of PCl_5 and x moles dissociate, at equilibrium we shall have $1 - x$ moles of PCl_5 and x moles of PCl_3 and x moles of Cl_2. The total number of moles present will be

$$(1 - x) + (x) + (x) = 1 + x$$

Each gas in this mixture exerts its own partial pressure independently of the other gases, and the exact magnitude of this pressure depends upon the amount of the gas present. Since we know the amount of each gas present and the total pressure, we can calculate the fraction of the total volume occupied by each gas and so calculate the partial pressure.

$$\text{Mole fraction of } PCl_5 = \frac{1 - x}{1 + x}$$

$$\text{Mole fraction of } PCl_3 = \frac{x}{1 + x}$$

$$\text{Mole fraction of } Cl_2 = \frac{x}{1 + x}$$

The partial pressure of each gas is the mole fraction of that gas multiplied by the total pressure, where P = total pressure

$$p_{PCl_5} = \frac{1-x}{1+x}P$$
$$p_{PCl_3} = \frac{x}{1+x}P$$
$$p_{Cl_2} = \frac{x}{1+x}P$$

Substituting these values in the equation, we get

$$K_p = \frac{\frac{x}{1+x}P \times \frac{x}{1+x}P}{\frac{1-x}{1+x}P} = \frac{\frac{x^2}{(1+x)^2}P^2}{\frac{1-x}{1+x}P}$$

$$K_p = \frac{\frac{x^2}{1+x}P}{(1-x)} = \frac{x^2P}{(1+x)(1-x)}$$

We know that PCl_5 at 250°C. and 1 atm. pressure is dissociated to the extent of 80 per cent. This means that x, the amount dissociated, is 0.8 and that P is 1 atm. Substituting these values, we get

$$K_p = \frac{(0.8)^2}{(1-0.8)(1+0.8)} (1)$$
$$K_p = \frac{(0.64)}{(0.2)(1.8)} = \frac{0.64}{0.36} = 1.778$$

From this value, let us calculate K_c. As we have seen on page 86, for this reaction

$$K_c = K_p \times \frac{1}{RT}$$
$$T = 273 + 250 = 523°\text{A.}$$
$$R = 0.0821 \text{ l.-atm.}$$
$$K_c = 1.778 \frac{1}{0.0821} \cdot \frac{1}{523}$$
$$K_c = 0.0414$$

Example 5.—Let us calculate K_p for the reaction

$$2HI \rightleftharpoons H_2 + I_2$$

For this reaction

$$_{H_2} \times$$

and from the gas laws

$$p = CRT$$

and

$$K_p = \frac{(C_{H_2} \times RT}{(C_{HI})^2(RT)^2} \qquad = \frac{C_{H_2} \times C_{I_2}}{(C_{HI})^2} \times \frac{(RT)^2}{(RT)^2}$$

therefore

$$K_p = K_c$$

Since we have previously calculated K_c, we need do no more.

REACTIONS BETWEEN SOLIDS

This heading usually prompts the questions: Do solids react with each other? Is not the reaction usually preceded by a change to the liquid state? These questions may best be answered by citing a simple experiment that can be verified with little trouble. If one takes solid potassium iodide and mixes it with solid mercuric nitrate and grinds them together in a mortar, one will observe that the mixture that was originally white becomes orange-red. In fact, it is not even necessary to grind them together; merely put them into a bottle, shake vigorously, and the mixture will change its color. The reaction that has taken place is the formation of mercuric iodide:

$$2KI + Hg(NO_3)_2 \rightarrow HgI_2 + 2KNO_3$$

Now that the fact that solid reactions take place has been verified, how can we explain them, knowing that the ions in these solids are relatively fixed in the crystal, *i.e.*, that they are vibrating around fixed points in the lattice? The explanation is not too difficult. It depends upon the bond energies, *i.e.*, the magnitude of the attractive force between the ions in the crystals.

When we rub two solids against each other, the ions at the surface of one crystal come into fairly close contact with the ions at the surface of the other crystal. If two of the ions in such a "collision" attract each other with a greater force than they do their original partners, they may break away from their old partnership and form new compounds. However, the process occurs only at the surface of the crystals, and soon the process will end because of the fact that the surfaces become completely used up. If we grind the compound, we break up the crystals, forming new surfaces that can react, and we also bring these new surfaces into more intimate contact with each other and thus form more of the new compound. Therefore, grinding potassium iodide and mercuric nitrate gives the mixture in the previous experiment a redder color than merely shaking them together.

Adhesion.—Many solids, when brought together, stick or adhere. The reason for this phenomenon is comprehensible if we consider that a solid reaction takes place at the points of contact between the two surfaces forming a compound. We do not usually consider this phenomenon as a type of compound formation, but adhesion is nevertheless a variety of compound formation that occurs at surfaces, and it is caused by the same forces that form compounds. Usually these forces are the secondary valence forces, or van der Waals' forces.

REACTIONS BETWEEN LIQUIDS

Pure liquids are not encountered too frequently in inorganic chemistry; especially is this true of elementary inorganic chemistry and work at normal temperatures. The notable exception is, of course, water. Liquids may be defined as substances in which the forces of thermal agitation have overcome the forces that maintain the crystal shape. Although permanent stable structures do not exist in liquids, temporary structures of short life do exist. The forces existing between the molecules are still large (compared to gases), and hence the molecules are close enough to each other so that their free paths are extremely small. In liquids, the molecules vibrate about a fixed position for a short while and then move to another position, where they again oscillate about a fixed point. It can thus be seen that liquids resemble both solids and gases. This similarity is further apparent in the reactions of liquids.

Before proceeding to the reactions of liquids, we should discuss the forces that hold liquids together. As is usual in chemical phenomena, the forces cannot be divided into classes as we divide sheep and goats, but we can describe the extremes of behavior. One extreme type of behavior is that exemplified by liquids in which the binding forces are electrostatic; *i.e.*, each particle, now called ion, has an electrical charge, either positive or negative. In such liquids, each ion is surrounded by an atmosphere of oppositely charged ions. However, none of these oppositely charged ions is firmly fixed in position, and none is close enough, except momentarily, to form a heteropolar bond. The atmosphere of oppositely charged ions that surrounds each ion is not fixed but varies at random. If we now add another liquid of the same type, several things may happen. First, if the liquids are added one to another slowly, they will form two layers and then slowly diffuse until they are thoroughly mixed. This diffusion in liquids is relatively slow compared to diffusion in gases and depends upon the viscosity of the liquid. The viscosity of a liquid or, in simpler language, the ease with which a liquid will flow, is only a measure of the forces of

attraction between the molecules. To demonstrate the slowness of diffusion in liquids, one can perform the following experiment. If one places some solid copper sulfate in the bottom of a cylinder and carefully fills the cylinder with water, the water will be colored blue about the crystals quite rapidly, but the blue color will progress up the cylinder very slowly, requiring a period of several weeks before the whole cylinder of liquid is colored.

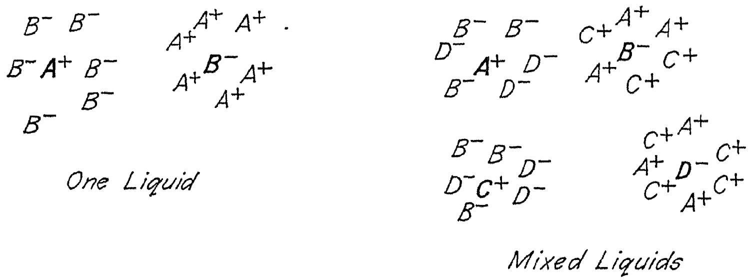


FIG. 34.—Atmospheres surrounding ions.

Let us now consider what happens when two liquids are mixed. Again we must deal with extremes; at one extreme nothing happens except that the atmospheres are now more heterogeneous than they previously were. The equation for this reaction can be written as

$$(A^+ + B^-) + (C^+ + D^-) \rightarrow A^+ + B^- + C^+ + D^-$$

The other extreme can be symbolized in an equation as

$$(A^+ + B^-) + (C^+ + D^-) \rightarrow A^+D^- + C^+B^-$$

or

$$(A^+ + B^-) + (C^+ + D^-) \rightarrow A^+D^- + C^+ + D^-$$

In this case, let us examine an ion A^+, surrounded by an atmosphere of B^- ions. Along comes an ion D^-, which moves into the atmosphere and, after an instant, grabs ion A^+ and holds it very tightly, at the same time repelling all the other negative ions that come into the vicinity. This is, of course, compound formation. If this happened every time an A^+ ion approached a D^- ion, the reaction would go to 100 per cent completion. Since we know that this does not occur, the description is justly labeled the extreme case. Actual substances fall between one extreme, where only heterogeneous atmospheres result, and the other extreme, where reactions go to completion.

We have thus far discussed liquids held together by electrostatic forces. At the other extreme are liquids held together by van der Waals' forces. In these liquids, the particles (molecules) are neutral,

and their arrangements are more complex than in purely ionic liquids. Reactions between two liquids of this type will vary according to the strength of the van der Waals' forces and the strength of the bonds in the molecule. However, since such liquids are only rarely encountered in qualitative analysis, we shall not discuss reactions between them. Suffice it to say that most real liquids fall somewhere between the two extremes, and hence most reactions between pure liquids are not too simple.

READING REFERENCES

GETMAN, FREDERICK N., and F. DANIELS: "Outlines of Theoretical Chemistry," 6th ed., John Wiley & Sons, Inc., New York, 1937.

LATIMER, W. M., and JOEL H. HILDEBRAND: "Reference Book of Inorganic Chemistry," rev. ed., The Macmillan Company, New York, 1940.

MARK, H.: "Physical Chemistry of High Polymeric Substances," Interscience Publishers, New York, 1940.

QUESTIONS

1. At 49.7°C. and 497.75 mm. pressure, N_2O_4 decomposes into NO_2 to the extent of 49.3%. Calculate K_c and K_p.

2. At 3000°C. and 1 atm. pressure, 40% of the molecules of CO_2 are decomposed into O_2 and CO. Calculate K_c and K_p.

3. The equilibrium constant of $2HI \rightleftharpoons I_2 + H_2$ is equal to 0.01984 at 448°C. If we start with 4 moles of hydrogen and 1 mole of iodine and permit the system to attain equilibrium, compute the concentrations of the components of the equilibrium mixture.

4. For the reaction $CaCO_3 \rightleftharpoons CaO + CO_2$, what would be the effect on the equilibrium of an increase in pressure?

5. For the reaction $2NH_3 \rightleftharpoons N_2 + 3H_2$, what would be the effect on the equilibrium of an increase in temperature?

6. Explain why paint sticks to a wall.

CHAPTER VII

REACTIONS OF CHEMICAL COMPOUNDS

II. REACTIONS WITH SOLVENTS

Although the reactions between pure gases, pure liquids, and pure solids are very interesting, they are not encountered too frequently in elementary inorganic chemistry. Most of the common reactions take place in aqueous solutions. However, before one can understand what happens during reaction in aqueous solutions, one must understand what happens when substances dissolve.

Solutions have been studied for a great many years, but the exact elucidation of the facts about solutions are still far from complete. However, we do understand—to a certain extent, at least—dilute solutions. We shall try to present here the modern views regarding the architecture—if it may be called that—of solutions.

Why Substances Dissolve.—We are sure that every chemist and student of chemistry has asked himself at some time or another, why, if I place substance A in water, will it dissolve, whereas if I place substance B in water, it will remain there unchanged? Of course, this question could be and was, in fact, answered simply for a long time in the following way. A substance dissolves because of its innate nature; or, to put it into other words, a substance dissolves because it is soluble. However, we know, and the chemists who gave this answer knew, that this was not an answer but only a dogmatic statement. Nevertheless, so little was known at that time that it was not profitable to pursue this question too far, since with only a scant handful of facts at their command, the chemists' answers soon degenerated into metaphysics and mysticism. Enough facts have been gathered at present, however, so that we can present a fairly intelligible picture of what happens when a substance is placed in a solvent.

Let us now take a concrete example. If we place a lump of copper sulfate in a beaker of water, we note that it dissolves gradually, turning the whole solution blue. We can ask, what has happened? Why does the copper sulfate dissolve? In the crystal of copper sulfate, we have a framework composed of tetraquocupric ions, $[Cu(H_2O)_4]^{++}$, and sulfate ions, $SO_4^{=}$, connected by a water bridge, thus giving the empirical formula $CuSO_4{\cdot}5H_2O$. A schematic drawing of the structure is shown

in Fig. 35. (Of course, this picture does not show the three-dimensional structure of copper sulfate or the other bonds that help it keep its three-dimensional form.)

The water molecules in the liquid water hit the molecules at the surface of the crystal, and, although many of them rebound, some of them stick and form a surface compound or layer. We know that this happens in most cases when a solid is in contact with a gas or a liquid. The reason for this adhesion of a layer of material is fairly easily explained. In the sulfate ion, the oxygen atoms are relatively negative as compared to the sulfur. In Fig. 36, these fractional charges are

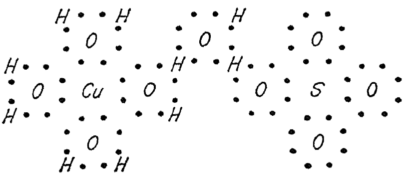


FIG. 35.—Schematic picture showing the water bridge between the two ions in $CuSO_4 \cdot 5H_2O$.

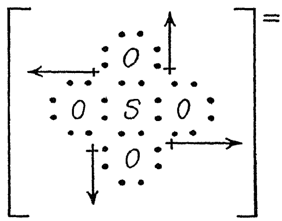


FIG. 36.—Dipoles within the $SO_4^{=}$ ion.

represented by arrows, the head being the negative and the tail being the positive end. Of course, the ion as a whole has a negative charge, and it is not a dipole, because the individual dipoles of the bonds are symmetrical and so cancel each other. However, each oxygen can attach itself, under propitious circumstances, to other dipoles, either permanent or induced. In the interior of the crystal, all these forces balance because of attached groups on all sides. However, at the surface, some of these forces are available, since certain sides of the ions are exposed and so can attach themselves to any available molecules or ions. Of course, Fig. 37 is only a two-dimensional picture and represents a very simple case, but it serves to show that at the surface there are forces available, both fractionally positive and negative. These forces attract a monomolecular film to the crystal. That film may, in turn, attract another film and so on, but the extra films do not usually stick so well as the first. This is the first step, and it happens whether the substance is soluble or not, just as long as the water will wet the solid. If the water does not wet the solid, then for some reason, the disposition of the forces at the surface is such that the solid is more or less indifferent to the water.

Since the molecules in the crystal are in constant vibration, at some time or another, some of the forces that were neutralized originally

in the body of the crystal attach themselves to solvent molecules; *i.e.*, molecules of water work their way between the ions and insulate them from each other, thus breaking the bonds holding them together. Finally, as this process continues, all the bonds are broken, and whole ions break away and, being surrounded by atmospheres of solvent molecules, are buffeted about and so diffused throughout the liquid.

Crystallization.—The reverse process also takes place. If enough of the dissolved ions are present in a solution, they will collide at intervals, and if the collision has the right energy and if the geometric

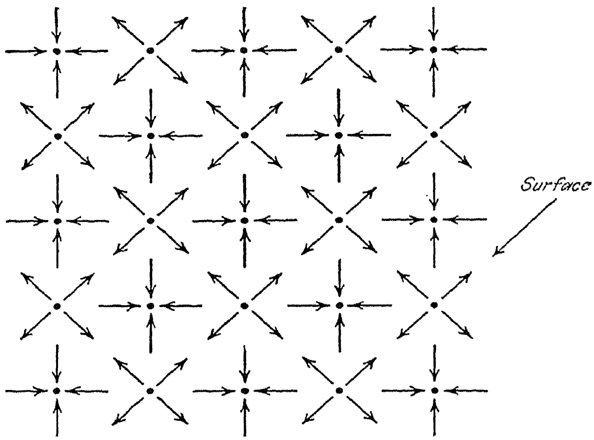


FIG. 37.—Schematic picture of internal and surface dipoles in a crystal.

conditions are right, they may squeeze out of the way some of the atmosphere surrounding each and so permit their forces to act upon one another. This bond may break during the next collision, but if sufficient ions are present in solution and their collisions are frequent enough, groups of ions will form. These groups of ions may grow in size, and if they reach a size of approximately 10^{-7} cm., they begin to appear as crystals. It is thus apparent that crystals have such definite shapes because they reflect the molecular distribution of forces.

Solubility.—When these two tendencies of the solid to dissolve and the ions to crystallize are equal, the solution is saturated. By adopting appropriate units, we may arrive at a figure that we call the solubility of the solid. This is usually expressed as the number of grams that can dissolve in a liter of water or the number of moles that can dissolve in a liter of solution; but other modes of expression may be used. However, solubility is merely a convenient method of measuring this equilibrium in the solution.

SOLUBILITY CALCULATIONS

Percentage Solutions:

Example 1.—How would you prepare a 50 per cent solution of $AgNO_3$? Dissolve 50 grams of $AgNO_3$ in 50 grams of water.

Example 2.—How would you prepare a 3 per cent solution of cadmium acetate? Dissolve 3 grams of cadmium acetate in 97 grams of water.

Molar Solution.—A $1M$ solution contains 1 gram mole of solute per liter of solution.

Example 3.—How would you prepare a $1M$ solution of $ZnSO_4 \cdot 6H_2O$? The molecular weight of $ZnSO_4 \cdot 6H_2O = 269.53$. Dissolve 269.53 grams of $ZnSO_4 \cdot 6H_2O$ in water, and make up to 1 liter of solution.

Example 4.—How many grams of $BaCl_2 \cdot 2H_2O$ are present in 27 ml. of a $1.34M$ solution? Molecular weight of $BaCl_2 \cdot 2H_2O = 244.31$. One liter will contain 1.34×244.31 grams, and 27 ml. will contain $\frac{27}{} \times 1.34 \times 244.31$ grams $= 8.84$ grams.

Molal Solution.—A 1 molal solution contains 1 mole of solute per 1,000 grams of solvent.

Example 5.—How would you prepare a 1.65 molal solution of KCl? Molecular weight of $KCl = 74.56$. Dissolve $1.65 \times 74.56 = 123.02$ grams of KCl in 1,000 grams of H_2O.

Example 6.—What weight of LiF is present in 110 grams of a 1.2 molal solution? Molecular weight of $LiF = 25.94$. 1.2×25.94 grams in 1,000 grams of $H_2O = 1{,}031.13$ grams. 31.13 grams of LiF $\approx$ 1,031.13 grams of solution,[1] x grams of LiF $\approx$ 110 grams of solution.[1]

$$\frac{31.13}{x} = \frac{1{,}031.13}{110}$$

$$x = \frac{31.13 \times 110}{1{,}031.13} = 3.32 \text{ g. of LiF}$$

Mole Fraction and Mole Per Cent.—In a 1 mole per cent solution of x, 1 per cent of the number of molecules present are x molecules.

Example 7.—How would you prepare a 1 mole per cent solution of LiF in water? Dissolve 1 mole $= 25.94$ grams of LiF in 99 moles $= 99 \times 18 = 1{,}782$ grams of water.

Example 8.—How would you prepare a 2.5 mole per cent solution of KCl in water? Dissolve 2.5 moles $= 2.5 \times 74.56 = 186.40$ grams of KCl in 97.5 moles $= 97.5 \times 18 = 1{,}755$ grams of H_2O.

[1] $\approx$ is read "is equivalent to" and means, for instance, that 31.13 grams of LiF are contained in 1,031.13 grams of solution.

Example 9.—What is the mole fraction and mole per cent of HCl in a 2.5 molal solution? Molecular weight of HCl = 36.46. There are present 2.5 moles of HCl for every 1,000/18 grams = 55.6 moles of water in a 2.5 molal solution.

$$\frac{2.5}{2.5 + 55.6} = \frac{2.5}{58.1} =$$
$$0.043 \times 100 = 4.3 \text{ mole per cent of HCl}$$

Normal Solutions.—A $1N$ solution of a substance contains one equivalent of the substance for every 1,000 ml. of solution.

For *acids, bases, and salts,* the equivalent is the molecular weight divided by: the valence number of the ion multiplied by the number of these ions present in the molecule.

For *oxidizing and reducing agents,* the equivalent is the molecular weight divided by: the valence change of the ion acting as an oxidizing or reducing agent multiplied by the number of such ions present in the molecule.[1]

Example 10.—Prepare a $1.75N$ solution of H_2SO_4. Molecular weight of H_2SO_4 = 98. Valence number of $SO_4^{=}$ = 2; number of $SO_4^{=}$ = 1; valence of H^+ = 1; number of H^+ = 2; valence number $\times$ no. = 2.

$$98/2 = 49 \text{ g./liter of solution} \approx 1N \text{ solution}$$
$$1.75N \approx 49 \times 1.75 = 85.75 \text{ g./liter solution}$$

Example 11.—Prepare a $0.0823N$ solution of $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, potassium antimonyl tartrate (tartar emetic). Molecular weight = 333.9. Valence number of K^+ = 1; number of K^+ = 1. Valence number of $(SbO)^+$ = 1; number of $(SbO)^+$ = 1. Valence number of $(C_4H_4O_6)^{=}$ = 2; number of $(C_4H_4O_6)^{=}$ = 1.

$$\frac{333.9}{1} \times 0.0823 = 27.48 \text{ g./liter of solution}$$

27.48 grams per liter is needed to make an $0.0823N$ solution of tartar emetic with respect to either the potassium or the antimonyl ion.

$$\frac{333.9}{2} \times 0.0823 = 13.74 \text{ g./liter of solution}$$

13.74 grams per liter is needed to make an $0.0823N$ solution of tartar emetic with respect to the tartrate ion.

Example 12.—How many grams of salt are present in 24.7 ml. of a $1.31N$ solution of K_2HPO_4? Molecular weight of K_2HPO_4 = 174.2;

[1] See Chap. IX for a thorough discussing of oxidation and reduction.

1 liter of a $1.31N$ solution contains 1.31 equivalent weights of solute.

$$24.7 \text{ ml. contains } \frac{24.7}{1000} \times 1.31 = 0.0324 \text{ equivalents of solute}$$

Equivalent weight of K_2HPO_4 with respect to $H^+ = 174.2$

$$\text{with respect to } K^+ = \frac{174.2}{2} = 87.1$$

$$\text{with respect to } PO_4^{\equiv} = \frac{174.2}{3} = 58.1$$

Hence, if the solution is $1.31N$ with respect to H^+, 24.7 ml. will contain

$$0.0324 \times 174.2 = 5.65 \text{ g.}$$

If the solution is $1.31N$ with respect to K^+, 24.7 ml. will contain

$$0.0324 \times 87.1 = 2.82 \text{ g.}$$

If the solution is $1.31N$ with respect to $PO_4^{\equiv}$, 24.7 ml. will contain

$$0.0324 \times 58.1 = 1.88 \text{ g.}$$

Example 13.—Prepare a $1.16N$ solution of $KMnO_4$. Molecular weight = 158. As a salt, a $1.16N$ solution contains

$$158 \times 1.16 = 183.3 \text{ g./liter}$$

As an oxidizing agent for the reaction $MnO_4^- \rightarrow Mn^{++}$, the change in valence number = 5. A $1.16N$ solution contains

$$158/5 \times 1.16 = 36.7 \text{ g./liter}$$

Normal solutions are most often used in quantitative analysis, since their use facilitates some of the necessary computations.

Specific Gravity.—One other method is often used to express solubility, *i.e.*, specific gravity. The specific gravity of a liquid at some temperature is the weight of a given volume of that liquid (at that temperature) divided by the weight of the same volume of water either at the same temperature or at some other reference temperature. It is usually written as follows:

$$\text{Sp. gr. } \frac{60°\text{F.}}{60°\text{F.}} \text{ of } 30.00\% \text{ HCl} = 1.1526$$

This means that the weight of the HCl solution was taken at 60°F. and was compared to the weight of an equal volume of water at 60°F. The quotient is 1.1526. Or it may be specified as follows:

$$\text{Sp. gr. } \frac{20°\text{C.}}{4°\text{C.}} \text{ of } 30\% \text{ HCl} = 1.1492$$

This means that the weight of the HCl solution was taken at 20°C. and was compared to the weight of an equal volume of water at 4°C. The quotient is 1.1492. Specific gravity is a very common method used in industry for specifying the concentrations of solutions. Tables can be found in the handbooks for a great number of common substances that convert specific gravities to percentage and various other units.

Example 14.—How many milliliters of HCl with a specific gravity $\frac{20°C.}{4°C.}$ of 1.1789 are needed to prepare 1,500 ml. of 0.52M HCl? From the tables, HCl sp. gr. $\frac{20°}{4°} = 1.1789$ corresponds to 36 per cent HCl and contains 424.4 grams HCl per liter. Molecular weight HCl = 36.46. Hence

$$\frac{424.4}{36.46} = 11.6 \text{ moles/liter}$$

36 per cent HCl solution is 11.6M

$$x = \frac{0.52(1{,}500)}{11.6} = 67.25 \text{ ml. of the HCl solution required}$$

Degree of Solubility.—Thus far we have discussed the case of substances that dissolve, but what about substances that do not dissolve? If the forces holding the solid together are sufficiently great, the solvent molecules may not be able to pull the solute particles into solution; or, to put it another way, by the time an ion has so disposed itself that it can be broken away from the solid, some ions that are already in solution will have collided with the surface and attached themselves to it. In other words, the equilibrium has been definitely shifted in one direction, toward crystallization. As a little thought will show, this point of view demands that all substances be soluble to some degree, even if the solubility is fantastically small.

Experimental Characteristics of Solutions.—One of the criteria by which we may classify solutions is their conductance of an electric current. In this classification, the extremes are, of course, solutions with no resistance to the passages of an electric current and solutions with infinite resistance to an electric current. Solutions exhibiting either of these two extreme types of behavior do not exist, but all the intermediate types do. Roughly, we can divide solutions into two classes: those that conduct very poorly and those that conduct very well, *i.e.*, nonelectrolytes and electrolytes.

Nonionic Solutions.—Let us first consider, briefly, nonelectrolytes. Here the solution is the so-called molecular solution; *i.e.*, the molecules

are present as such in the solution. In dissolving a solid that forms solutions of this type, the solvent usually acts against the van der Waals' forces that hold such a crystal together. If the solution is very dilute, it resembles a gas in its behavior; *i.e.*, the solute molecules are so far apart and collide with each other so infrequently (relatively speaking) that we may think of the solution as a gas having solvent molecules instead of just space between the solute molecules. Solutions of this type may be dealt with mathematically in a manner reminiscent of gases. If the solution becomes more concentrated, the interaction between solvent and solute molecules becomes more complex, and such solutions are not dealt with so easily. However, we shall not consider the reactions of this type of solution.

Ionic Solutions.—We shall consider, rather, solutions that conduct the electric current; *i.e.*, solutions in which the solute exists as ions, electrically charged bodies, and solutions in which the solute exists both in the form of molecules and ions. If we take two strips of litmus paper, one red and one blue, and place them in a solution of this type, one of three things will happen. Either the color of the blue strip will become red or the color of the red strip will become blue or the color of both strips will remain unchanged. Furthermore, if we take the solution that turns blue litmus red and add it to the solution that turns red litmus blue, after a certain amount has been added, the resulting solution will no longer change the color of litmus; *i.e.*, the two solutions will have neutralized each other. These differences in ionic solutions have been known for a very long time and have been given special names. Solutions that turn blue litmus red are called acidic solutions; solutions that turn red litmus blue are called basic, or alkaline, solutions. Solutions that do neither are called neutral solutions. Acidic solutions will neutralize basic solutions and vice versa.

THE MODERN THEORY OF ACIDITY AND BASICITY

Let us see why certain substances, when dissolved in a solvent, give rise to acidic solutions, why certain others give rise to basic solutions, whereas still others yield neutral solutions.

Aqueous Solutions.—Let us take an actual example. If we dissolved some sulfur trioxide, SO_3, which is a solid, in water, the sulfur trioxide would dissolve and, because of the intermolecular forces, would react with water molecules thus:

$$3H_2O + SO_3 \rightarrow 2H_3O^+ + SO_4^=$$

(Of course, we are not showing the existence of the whole atmosphere of water molecules surrounding each ion in this case.) If we tested this solution, we should find that it was acidic.

Let us take another example. If we dissolved some metallic sodium, Na, in water, the sodium would dissolve, and the reaction would occur as follows:

$$2Na + yH_2O \rightarrow 2Na(H_2O)_x^+ + 2\ OH^- + H_2 \uparrow$$

Testing this solution with litmus would show that it is basic.

Let us now take these two solutions, one basic and the other acidic, and heat them, thereby evaporating the excess water. After a while, in the case of the basic solution, we should have left a white solid, whereas in the case of the acidic solution, we should have an oily liquid. By analysis, we could show that these substances have a composition corresponding to the formulas $NaOH$ and H_2SO_4, respectively. These substances are evidently different from the parent compounds. However, these compounds when dissolved in water give solutions that are basic and acidic, just like the original solutions. Let us now add one solution to the other until the resulting solution is neutral and then evaporate the water. By this process, we obtain a white solid, which, on analysis, is found to have the formula Na_2SO_4. This substance, on re-solution, gives a solution neutral to litmus.

At this point, the student probably wonders how all this is to be explained. Let us set down again all the reactions that have been studied.

Acidic solution:

$$SO_3 + 3H_2O \rightarrow 2H_3O^+ + SO_4^=$$
$$2H_3O^+ + SO_4^= + xsH_2O \underset{\Delta}{\rightarrow} xsH_2O \uparrow + H_2SO_4$$
$$H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + SO_4^=$$

Basic solution:

$$2Na + yH_2O \rightarrow 2Na(H_2O)_x^+ + 2OH^- + H_2 \uparrow$$
$$Na(H_2O)_x^+ + OH^- + xsH_2O \underset{\Delta}{\rightarrow} xsH_2O \uparrow + NaOH$$
$$NaOH + yH_2O \rightarrow Na(H_2O)_x^+ + OH^-$$

For the neutralization, the reaction would be:

$$[2Na(H_2O)_x^+ + 2OH^-] + [2H_3O^+ + SO_4^=] \rightarrow$$
$$2Na(H_2O)_x^+ + SO_4^= + 4H_2O$$

Neutral solution:

$$2Na(H_2O)_x^+ + SO_4^= + 4H_2O \underset{\Delta}{\rightarrow} Na_2SO_4 + xsH_2O \uparrow$$
$$Na_2SO_4 + xH_2O \rightarrow 2Na(H_2O)_x^+ + SO_4^=$$

Let us now examine these equations. What differences exist between the neutral and the acidic and the basic solutions? What has

happened in the course of the neutralization? The most important thing that has happened is that the hydronium ion H_3O^+ has combined with the hydroxyl ion, OH^-, and reformed some molecules of solvent. If we examine the neutralization of many different types of aqueous acidic and basic solutions, we shall find that they are all accompanied by the formation of water molecules from the hydroxyl and hydronium ions present. We may say, therefore, that in aqueous solutions, the presence of hydronium ions will give the solution an acidic character, whereas the presence of hydroxyl ions will give it a basic character.

Liquid Ammonia Solutions.—Let us now consider the same phenomena in a nonaqueous solvent, *e.g.*, liquid ammonia. Liquid ammonia is colorless and boils at $-33.40°C.$ at atmospheric pressure. If we dissolved some sodium in this solvent, the reaction would be

$$2Na + yNH_3 \rightarrow 2Na(NH_3)_x^+ + 2NH_2^- + H_2\uparrow$$

and the solution would be basic. Let us make another solution by dissolving H_2SO_4, secondary hydrogen sulfate, in liquid ammonia. The reaction would be

$$H_2SO_4 + 2NH_3 \rightarrow 2NH_4^+ + SO_4^=$$

and the solution would be acidic.

These two solutions can be added to one another (in the presence of an indicator to indicate the point of neutrality), and they will neutralize one another. The reaction would be

$$[2Na(NH_3)_x \quad 2NH_2^-] + [2NH_4^+$$
$$2Na(NH_3)_x^+ + SO_4^= \quad 4NH_3$$

Again, as in the case of aqueous solutions, neutralization has been accomplished by the reforming of neutral solvent molecules from two ionic fragments.

If we took the original acidic solution and evaporated the solvent, we should get a substance $(NH_4)_2SO_4$, ammonium sulfate, which would give an acidic solution upon re-solution in liquid ammonia.

$$2NH_4^+ + SO_4^= + xsNH_3 \xrightarrow[\Delta]{} (NH_4)_2SO_4 + xsNH_3\uparrow$$
$$(NH_4)_2SO_4 + xsNH_3 \rightarrow 2NH_4^+ + SO_4^= + xsNH_3$$

The basic solution would also give a solid upon evaporation that, when redissolved, would give a basic solution.

$$Na(NH_3)_x^+ + NH_2^- + xsNH_3 \xrightarrow[\Delta]{} \underset{\text{sodamide}}{NaNH_2} + xsNH_3\uparrow$$
$$NaNH_2 \quad ;sNH_3 \rightarrow Na(NH_3)_x^+ + NH_2^- + xsNH_3$$

Selenium Oxychloride Solutions.—Let us now choose another solvent, selenium oxychloride, This solvent is a liquid that is

very reactive, attacking most substances. It is inert to platinum, glass, and tungsten. Note, however, that no hydrogen exists in this solvent. Let us dissolve some sulfur trioxide in selenium oxychloride. The reaction would be

$$SO_3 + 2SeOCl_2 \rightarrow [(SeOCl_2)(SeOCl)]^+ + SO_3Cl^-$$

Let us also prepare a solution by dissolving sodium in selenium oxychloride. The reaction would be

$$6Na + 4SeOCl_2 \rightarrow 6Na^+ + 6Cl^- + 2SeO_2 + Se_2Cl_2$$

If we added one of these solutions to the other, we should find that at some point neutrality exists (although here we would follow the course of the reaction electrically by means of conductance rather than with an indicator). The reaction for this neutralization would be written thus:

$$\{SO_3Cl^- + [(SeOCl_2)(SeOCl)]^+\} + \{Na^+ + Cl^- + \\ Na^+ + SO_3Cl^- +$$

Definition of Acidic and Basic Solutions.—Let us now set down the neutralization reactions in each of the three systems that we have examined:

Water system:

$$(2Na^+ + 2OH^-) + (2H_3O^+ + SO_4^=) \rightarrow 2Na^+ + SO_4^= + xsH_2O$$

Ammonia system:

$$(2Na^+ + 2NH_2^-) + (2NH_4^+ + SO_4^=) \rightarrow 2Na^+ + SO_4^= + xsNH_3$$

Selenium oxychloride system:

$$\{Na^+ + Cl^-\} + \{SO_3Cl^- + [(SeOCl_2)(SeOCl)]^+\} \rightarrow \\ Na^+ + SO_3Cl^- + xsSeOCl_2$$

We can see that these reactions resemble each other; in fact, the parallelism existing is quite remarkable. For each solvent, the acidic solution contains a negative ion of some sort plus a positive ion that came from the solvent, whereas the basic solution contains a positive ion of some sort plus a negative ion that came from the solvent. During neutralization, the negative and positive ions that came from the solvent recombined to form more solvent, leaving the other ions unchanged in solution. The ions that came from the solvent may be called solvo-ions; *i.e.*, in the case of *acidic aqueous* solutions, the solvo-ion is the hydronium ion; in the case of the *basic liquid ammonia* solutions, the solvo-ion is the amido ion NH_2^-. Hence one can say

that **an acidic solution is one that contains as one of the predominant species present a positive solvo-ion,** and **a basic solution is one that contains as one of the predominant species present a negative solvo-ion.** During neutralization, the negative solvo-ions combine with the positive solvo-ions to form neutral solvent molecules. Hence **a neutral solution is one in which none of the predominant species present is a solvo-ion.**

Limited Definition for Water Solutions.—Since most elementary work deals only with water solutions, we can present a version of this definition that applies only to aqueous solutions. In the water system, the positive solvo-ion is the hydronium ion, and the negative solvo-ion is the hydroxyl ion; hence **in a water solution, if the hydronium ion H_3O^+ is one of the predominant species present, the solution is acidic; if the hydroxyl ion OH^- is one of the predominant species present, the solution is basic.**

NOTE: The reader may have noticed that we avoid the use of the words acid and base, preferring to speak about acidity and basicity. By doing this, we think that a rather large controversy as to what to call an acid and what to call a base can be avoided. Confining the definitions to solutions also has its advantages. If the current theories of acids and basis are followed, through the theories of Bronsted-Lowry, G. N. Lewis and Usanowitch, one discovers that in this way the subject of acids and bases is so expanded as to include practically the whole of chemical reaction. Hence the need for choosing a halting point is apparent.

If we deal historically with the problem, we find that acidity and basicity are best known in solution and most commonly used in connection with solutions, hence it seems wise to call a halt there. Furthermore, if we discard the nomenclature, acid and base, we find that the problem is immensely simplified, and the fact that both zinc chloride and hydrogen chloride give acidic solutions is not too difficult to understand. Similarly, the facts regarding the acidity and basicity of salt solutions become clear. The only drawback in the whole picture is the name that we now give to hydrogen compounds, calling hydrogen chloride in water solution hydrochloric acid and anhydrous secondary hydrogen sulfate, sulfuric acid. We hope, however, that in time the anachronism will disappear, as have the early types of nomenclature. In passing, may we state that although in this chapter we have adhered strictly to the policy of not using the words acid and base, we have not been so strict in other parts of this book, since we believe that it is always wise to make haste slowly, *i.e.*, not to be too dogmatic about introducing changes.

Substances That Give Acidic, Basic, and Neutral Solutions.—The logical question now is, can we predict whether a certain substance will give an acidic, basic, or neutral solution? And as a corollary, how acidic or basic will the solution be? We shall confine our discussion here to aqueous solutions, since they are the ones most frequently encountered; however, the principles developed may readily be extended to include nonaqueous solutions.

Let us again review our definition of an acidic and of a basic solution. In a water solution, if the hydronium ion H_3O^+ is one of the predominant species present, the solution is acidic; if the hydroxyl ion OH^- is one of the predominant species present, the solution is basic. There are several principles embodied in this definition.

1. *The substance must be soluble at least to some extent.* This statement is fairly obvious, since a substance must dissolve if we are to have a solution.

2. *The substance must react with the solvent, the reaction involving some primary valence bonds and yielding ions.*

3. *One of the predominant species present as the result of the reaction must be the hydronium ion if the solution is to be acidic or the hydroxyl ion if the solution is to be basic.*

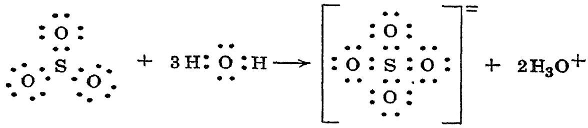
Let us now examine these criteria further and see what the underlying reasons are for these differences in behavior. A substance may dissolve for one of two reasons. (1) The substance will react with the solvent, thereby involving the secondary valence forces. This type of reaction is a sort of addition reaction and will not give rise to ions. Or (2) the substance may react involving the primary valence forces and liberating ions. Let us examine further this second case. Notice that the statement was conditional, "The substance may react." What, exactly, determines if it will react? The determining factor is the **bond strength,** *i.e.*, the magnitude of the force of attraction between the atoms. Let us choose several actual cases and see how this works.

BOND STRENGTH

Oxy Compounds.—Let us choose first sodium oxide, Na_2O, which is quite soluble. The attraction between the sodium and the oxygen atoms is not great, and the energy required to separate them is not very great. Hence water can react with this "molecule" and separate the ions thus:

$$\mathrm{Na}:\ddot{\underset{..}{\mathrm{O}}}:\mathrm{Na} + xs\mathrm{H}:\ddot{\underset{..}{\mathrm{O}}}:\mathrm{H} \rightarrow 2\mathrm{Na}(\mathrm{H_2O})_x^+ + 2[:\ddot{\underset{..}{\mathrm{O}}}:\mathrm{H}]^-$$

Since this reaction furnishes OH^- ions, the solution will be basic. Let us compare the reaction of this compound with silicon dioxide. In silicon dioxide, the attraction between the silicon and oxygen is very great, and hence it is difficult to separate the ions. Therefore SiO_2 is insoluble. On the other hand, in sulfur trioxide, SO_3 (which is a white solid), the oxygen is very strongly bound to the sulfur, and the energy required to separate them is very great. In fact, the sulfur has such an avidity for oxygen that it will break up the water and remove oxygen from it as



Since this reaction furnishes hydronium ions, the solution is acidic. In these three examples, we have examined a few members of a horizontal line or period in the atomic table, and we have seen that, although small energies are required to separate the atoms in the first groups, as we proceed to the right, the elements not only will not give up their partners readily but will, in fact, break up other compounds so that they can share more electrons.

One other factor (except the group of the periodic table) influences the bond strength. This is the period in which the element is placed, or, to put it another way, the atomic volume. As the atomic number increases, the number of shells surrounding the atoms increases, or the volume of the atoms increases. Since the binding forces are electrical, they depend upon the magnitude of the charges and the distance. This point is illustrated by the fact that, whereas beryllium oxide, BeO, is insoluble and magnesium oxide, MgO, is slightly soluble, calcium oxide reacts completely with water, forming calcium hydroxide. These rules do not, unfortunately, hold exactly in the later periods; other factors enter that complicate the picture.

Hydro Compounds.—The hydrides are another and simpler example of the influence of bond strength. When sodium hydride is dissolved, the sodium ion and the hydride ion are separated, and the latter reacts with the water to give hydrogen molecules and hydroxyl ions, resulting in a basic solution.

Step 1: $\mathrm{Na{:}H} \xrightarrow[\mathrm{H_2O}]{xs} \mathrm{Na^+} + (\mathrm{H}{:})^-$

Step 2: $(\mathrm{H}{:})^- + \mathrm{H{:}\ddot{\underset{\cdot\cdot}{O}}{:}H} \rightarrow \mathrm{H{:}H}\uparrow + [{:}\ddot{\underset{\cdot\cdot}{\mathrm{O}}}{:}\mathrm{H}]^-$

Over-all reaction: $\mathrm{Na{:}H} + \mathrm{H{:}\ddot{\underset{\cdot\cdot}{O}}{:}H} \rightarrow \mathrm{H{:}H}\uparrow + \mathrm{Na^+} + [{:}\ddot{\underset{\cdot\cdot}{\mathrm{O}}}{:}\mathrm{H}]^-$

At the other end of this period, we have hydrogen chloride, HCl. This compound reacts with water, and the electrons are attached not to the hydrogen but to the chlorine; so we get a hydronium ion and a chloride ion, giving an acidic solution.

$$\mathrm{H{:}\ddot{\underset{\cdot\cdot}{Cl}}{:}} + \mathrm{H{:}\ddot{\underset{\cdot\cdot}{O}}{:}H} \rightarrow [{:}\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}{:}]^- + \mathrm{H_3O^+}$$

In between these two, we have methane, CH_4, in which the bond

strength is high, and accordingly, this compound is not appreciably soluble in water.

Hydroxy Compounds.—Here we have an interesting case. Let us take a hypothetical compound, ROH, which could react in one of three ways if added to water.

1. The bond between the oxygen and the element R could split, giving a basic solution.

$$ROH + H_2O \rightarrow R(H_2O)_x^+ + OH^-$$

This would happen if the strength of the bond between the R and the O was weaker than the bond between the O and the H. An actual example of this is sodium hydroxide, NaOH.

$$NaOH + xH_2O \rightarrow Na(H_2O)_x^+ + OH^-$$

2. The bond between the oxygen and hydrogen could break, giving an acidic solution.

$$ROH + H_2O \rightarrow RO^- + H_3O^+$$

This would happen if the OH bond were weaker than the RO bond. An actual example of this is hypochlorous acid, HOCl.

$$HOCl + H_2O \rightarrow H_3O^+ + ClO^-$$

3. The third alternative is that it will not react at all.

$$ROH + H_2O \rightleftharpoons ROH + H_2O$$

An example of this is methyl alcohol, CH_3OH.

Amphoteric Substances.—In addition to these three types of behavior, there are many other substances that can react in both ways; *i.e.*, either the OH or the OR bond can be broken.

$$ROH + H_2O \begin{cases} \nearrow RO^- + H_3O^+ \\ \searrow R(H_2O)_x^+ + OH^- \end{cases}$$

In these cases, exactly which type of behavior will occur will depend entirely upon what other ions are present in the solution. Stannous hydroxide, $Sn(OH)_2$, which is not very soluble in water, is a substance of this sort. If we add stannous hydroxide to a solution containing hydronium ions, the SnO bond will break, but if we add it to a solution containing hydroxyl ions, the OH bond will break.

$$Sn(OH)_2 + 2H_3O^+ \xrightarrow[xsH_2O]{xsH_3O^+} Sn^{++} + 4H_2O$$

$$Sn(OH)_2 + 2OH^- \xrightarrow[xsH_2O]{xsOH^-} SnO_2^{--} + 2H_2O$$

This particular reaction is utilized in the laboratory in order to prepare sodium stannite solution. Sodium hydroxide is added dropwise to a

stannous chloride solution until stannous hydroxide precipitates. Then an excess of sodium hydroxide is added, and the stannous hydroxide dissolves, forming sodium stannite. Since many of the ions that are encountered in the course of an analysis are distinctly amphoteric, these properties are often utilized to effect separations. As an example, the separation of aluminum from iron may be cited. If we treat a mixture of aluminum and ferric ions with sodium hydroxide, the first reaction is the separation of the hydroxides.

$$Fe^{+++} + Al^{+++} + 6OH^- + H_2O \rightarrow Fe(OH)_3(H_2O)_x + Al(OH)_3(H_2O)_y$$

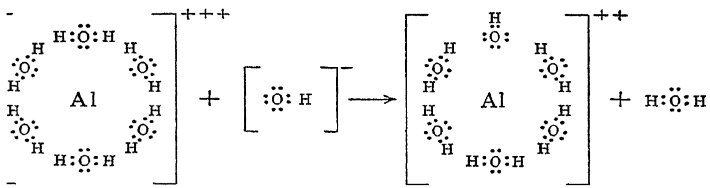
If now we treat these hydroxides with an excess of sodium hydroxide, the aluminum dissolves, forming the aluminate ion and leaving ferric hydroxide behind.

$$Fe(OH)_3(H_2O)_x + xsOH^- \rightarrow \text{no reaction}$$
$$H_2O)_y + xsOH^- \rightarrow AlO_2^- + xsOH^- + xsH_2O$$

It is interesting to investigate the probable mechanism of this latter reaction. Let us start with the triply positive aluminum ion and add hydroxyl ions and see what happens.

$$Al(H_2O)_6^{+++} + OH^- \rightarrow Al(OH)(H_2O)_5^{++} + H_2O$$

ısing the electronic symbolism

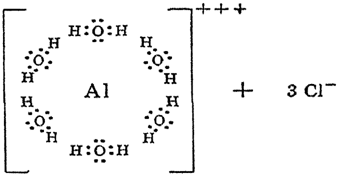


The next steps would be

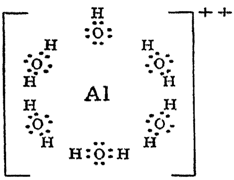
$Al(OH)(H_2O)_5^{++} + OH^- \rightarrow Al(OH)_2(H_2O)_4^{+} + H_2O$
$Al(OH)_2(H_2O)_4^{+} + OH^- \rightarrow Al(OH)_3(H_2O)_3^{0} + H_2O$ *precipitate*
$Al(OH)_3(H_2O)_3^{0} + OH^- \rightarrow Al(OH)_4(H_2O)_2^{-} + H_2O$
$Al(OH)_4(H_2O)_2^{-}$ is equivalent to $AlO_2(H_2O)_4^{-}$, *which is the meta aluminate ion*

Beautiful as this mechanism looks, however, the student should not be misled into thinking that it represents the whole truth. It really does not. It represents certain aspects of it. Let us examine the facts and see what we can gather from them. From analytical data, we know that aluminum chloride usually crystallizes as the hexahydrate and accordingly has the formula $AlCl_3 \cdot 6H_2O$. This has been interpreted to mean that the aluminum ion coordinates six atoms of water and that,

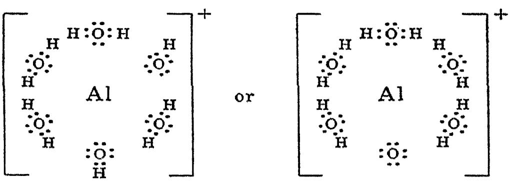
the chloride ions are held by heteropolar bonds. Hence the symbolic picture would be



When the hexaquo-aluminum ion reacts with a hydroxyl ion, one of the hydrogens is removed, and the picture is

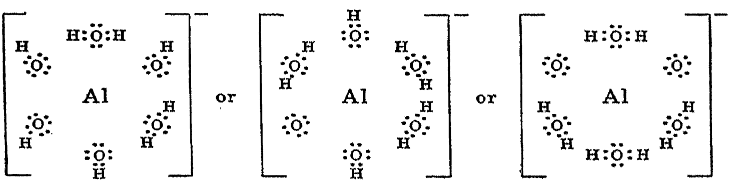


However, the oxygen, which has only one hydrogen atom attached to it, is not located uniquely, and an interchange or migration of hydrogen atoms may occur. If we remove two hydrogen atoms by reaction with two hydroxyl ions, we can draw two alternate pictures.



Any two of the oxygen atoms may have only one H each.

Either of these can exist, and both probably do exist in equilibrium with each other. Similarly, if we remove four hydrogen atoms, we have the following pictures:



All of these probably exist in equilibrium with each other. In solution,

the structure $[Al(OH)_4(H_2O)_2]^-$ probably predominates. If, however, one dehydrates the solution by evaporation of the water, since the form $[AlO_2(H_2O)_4]^-$ can lose the most water, the equilibrium is shifted in that direction, and the final dry product is $NaAlO_2$; hence the common formulation of the aluminate ion as AlO_2^-.

General Conclusions.—We thus see that we can predict in the case of hydro, hydroxy, and oxy compounds of the elements what reaction with H_2O will take place. The general prediction will be that compounds whose central atoms are in the first groups of the periodic table will be basic, whereas those in the last groups will be acidic, and those in the intermediate groups will be either inert or amphoteric.

SOLUTIONS OF SALTS

It is also of interest to see whether we can predict whether a solution of a salt will be acidic, basic, or neutral. The answer is that to some extent we can. Let us take some examples:

1. We wish to predict what sort of solution sodium chloride will give when dissolved in water. The first reaction would be the separation of the ions.

$$Na^+Cl^- + xsH_2O \rightarrow Na(H_2O)_x^+ + Cl^-$$

As we know from previous discussions and reactions, the sodium ion does not react with water (except to form a complex ion). Similarly, the chloride ion does not react with water. Hence the solution would be neutral.

2. We wish to predict what sort of solution sodium cyanide, Na^+CN^-, will give. First let us separate the ions.

$$Na^+CN^- + xsH_2O \rightarrow Na(H_2O)_x^+ + CN^-$$

The sodium ion does not react with water, but the cyanide ion does; thus

$$CN^- + H_2O \rightarrow HCN + OH^-$$

Hence the solution will be basic.

3. As a third illustration, we wish to predict what sort of solution we shall get with ammonium chloride, NH_4Cl.

$$NH_4^+Cl^- + xsH_2O \rightarrow NH_4^+ + Cl^- +$$

The chloride ion does not react with water, but the ammonium ion does.

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$$

Hence the solution would be acidic.

4. Let us take still another example, ammonium acetate, $NH_4C_2H_3O_2$.

$$NH_4{}^+C_2H_3O_2{}^- + xsH_2O \rightarrow NH_4{}^+ + C_2H_3O_2{}^- + xsH_2O$$

Here both ions react with water.

$$(a)\ NH_4{}^+ + H_2O \rightarrow NH_3 + H_3O^+$$
$$(b)\ C_2H_3O_2{}^- + H_2O \rightarrow HC_2H_3O_2 + OH^-$$

and

$$H_3O^+ + OH^- \rightarrow H_2O + \left\{\begin{array}{l}\text{some } OH^- \text{ or}\\ \text{some } H_3O^+ \text{ or}\\ \text{neither}\end{array}\right.$$

Whether the final solution will be weakly acidic or weakly basic or neutral will depend entirely upon which reaction, (*a*) or (*b*), goes further to completion. In other words, it will depend upon the equilibrium constants. Let us write these equilibrium constants.
For (*a*)

where $[NH_3]$ = concentration of ammonia, etc.
or, since the concentration of the water is essentially constant

For (*b*)

$$k' = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2{}^-][H_2O]}$$

or

$$K' = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2{}^-]} = k'[H_2O]$$

It can be seen from these equations that if the reaction in equation (*a*) goes further to the right than does reaction (*b*), K will be greater than K', and hence the solution will be acidic and vice versa. In this particular case, K and K' are approximately equal, and the solution is neutral.

Therefore, in the case of the simpler salts, we may list four cases:

I. Neither the cation nor the anion reacts with water. The solution therefore is neutral.

II. The anion but not the cation reacts with water. The solution is basic.

NOTE: If the substance being dissolved already possesses hydroxyl ions in its structure and these ions are separated by the water, the solution will be basic, since there is thus an increase in the number of hydroxyl ions present.

Example:

$$NaOH + xsH_2O \rightarrow Na(H_2O)_x^+ + OH^-$$

III. The cation but not the anion reacts with water. The solution is acidic.

NOTE: If the substance being dissolved already possesses hydronium ions in its structure and these ions are separated by the water, the solution will be acidic, since there is thus an increase in the number of hydronium ions present. *Example:*

$$H_2SO_4 \cdot 2H_2O \equiv (H_3O)_2SO_4$$
$$(H_3O)_2SO_4 + xsH_2O \rightarrow 2H_3O^+ + SO_4^= + xsH_2O$$

IV. If both the cation and the anion react with water, the solution may be acidic, basic, or neutral, depending upon which reaction goes further to completion.

Reactions of this type, *i.e.*, reactions of salts with water, are generally called hydrolytic reactions, or hydrolysis.

More Complicated Cases of Salt Solutions.—We have thus far considered anions and cations that react with water in one way, but there are ions that can react in more than one way, *e.g.*, the orthophosphate ions. Let us consider first hydrogen phosphate, H_3PO_4, and its water solution. The first reaction is

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + \underset{\substack{\text{Secondary}\\ \text{orthophos-}\\ \text{phate ion}}}{H_2PO_4^-} \tag{1}$$

and the solution is acid. The equilibrium constant for this reaction is

$$k = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4][H_2O]}$$
$$k[H_2O] = K = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 1.1 \times 10^{-2}$$

The $H_2PO_4^-$ ion can react further in two ways:

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^= \tag{2}$$
$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^- \tag{3}$$

However, reaction (3) does not go appreciably from the left to the right but, rather, from the right to the left. Reaction (2) proceeds to some extent. The equilibrium constants are

$$K' = \frac{[H_3O^+][HPO_4^=]}{[H_2PO_4^-]} = 2.0 \times 10^{-7}$$
$$K'' = \frac{[OH^-][H_3PO_4]}{[H_2PO_4^-]} = 0.91 \times 10^{-12}$$

K' is greater than K''; therefore reaction (2) predominates.

The $HPO_4^{=}$ ion can react further; thus

$$HPO_4^{=} + H_2O \begin{cases} \rightleftharpoons H_3O^+ + PO_4^{\equiv} & (4) \\ \rightleftharpoons H_2PO_4^- + OH^- & (5) \end{cases}$$

Reaction (5) is predominant, as may be seen from the equilibrium constants

$$K''' = \frac{[H_3O^+][PO_4^{\equiv}]}{[HPO_4^{=}]} = 3.6 \times 10^{-13}$$
$$K'''' = \frac{[OH^-][H_2PO_4^-]}{[HPO_4^{=}]} = 5.0 \times 10^{-8}$$

and K'''' is greater than K'''.

The final ion $PO_4^{\equiv}$ can react in only one way.

$$PO_4^{\equiv} + H_2O \rightleftharpoons HPO_4^{=} + OH^- \qquad (6)$$

and the equilibrium constant is

$$K''''' = \frac{[OH^-][HPO_4^{=}]}{[PO_4^{\equiv}]} = 2.78 \times 10^{-2}$$

Let us see how this may be applied to the phosphate salts. If we dissolve primary sodium orthophosphate, NaH_2PO_4, in water, what sort of solution will we get?

$$NaH_2PO_4 + xsH_2O \rightarrow Na(H_2O)_x^+ + H_2PO_4^-$$
$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{=} \qquad (7)$$

This reaction is the same as (2) and would predominate; hence the solution would be acid. If we dissolve secondary sodium orthophosphate, Na_2HPO_4, in water, the reaction will be

$$Na_2HPO_4 + xsH_2O \rightarrow 2Na(H_2O)_x^+ + HPO_4^{=}$$
$$HPO_4^{=} + H_2O \begin{cases} \rightleftharpoons H_2PO_4^- + OH^- & (8) \\ \rightleftharpoons PO_4^{\equiv} + H_3O^+ & (9) \end{cases}$$

Since (8) is the predominant reaction, as can be seen from the equilibrium constant, the solution will be basic. If we dissolve tertiary sodium orthophosphate, Na_3PO_4, in water, the reaction will be

$$Na_3PO_4 \xrightarrow{xsH_2O} 3Na(H_2O)_x^+ + PO_4^{\equiv}$$
$$PO_4^{\equiv} + H_2O \rightleftharpoons HPO_4^{=} + OH^- \qquad (10)$$

and

$$+ H_2O \rightleftharpoons H_2PO_4^- + OH^- \qquad (11)$$

Hence the solution would be basic and more basic than the solution of secondary sodium orthophosphate, since there are more hydroxyl ions formed.

TABLE XV.—IONIZATION CONSTANTS

	K	Degrees centigrade
$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$	1.8×10^{-5}	20
$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$	4.3×10^{-7}	20
$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^=$	4.7×10^{-11}	20
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	7.2×10^{-10}	25
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.5×10^{-4}	20
$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$	1.1×10^{-2}	18
$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^=$	2×10^{-7}	18
$HPO_4^= + H_2O \rightleftharpoons H_3O^+ + PO_4^{\equiv}$	3.6×10^{-13}	18
$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$	9×10^{-8}	25
$HS^- + H_2O \rightleftharpoons H_3O^+ + S^=$	1.2×10^{-15}	25
$H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^-$	1.7×10^{-2}	25
$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^=$	5×10^{-6}	25
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	3.7×10^{-8}	17
$HN_3 + H_2O \rightleftharpoons H_3O^+ + N_3^-$	1.9×10^{-5}	25
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.75×10^{-5}	20
$Zn(OH)_2 + 6H_2O \rightleftharpoons Zn(H_2O)_6^{++} + 2OH^-$	1.5×10^{-9}	25

Another type of reaction is that given by zinc chloride, which, upon solution, yields

$$ZnCl_2 + xsH_2O \rightarrow Zn(H_2O)_6^{++} + 2Cl^-$$

The chloride ion does not react appreciably with water, but the hexa-aquozinc ion does.

$$Zn(H_2O)_6^{++} + H_2O \rightleftharpoons [Zn(OH)(H_2O)_5]^+ + H_3O^+$$

Hence the solution is acid. Many other salts act in the same manner, *e.g.*, aluminum chloride, $AlCl_3$.

$$AlCl_3 + xsH_2O \rightarrow Al(H_2O)_6^{+++} + 3Cl^-$$
$$Al(H_2O)_6^{+++} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{++} + H_3O^+$$

If we gradually remove the hydronium ions by adding hydroxyl ions, the reaction is driven to the right in an attempt to maintain the equilibrium, and after a while, insoluble $Al(OH)_3(H_2O)_3$ is precipitated.

$$[Al(H_2O)_5(OH)]^{++} + H_2O \rightleftharpoons [Al(H_2O)_4(OH)_2]^+ + H_3O^+$$
$$[Al(H_2O)_4(OH)_2]^+ + H_2O \rightleftharpoons [Al(OH)_3(H_2O)_3]^0 + H_3O^+$$

In many cases, it is not even necessary to remove the hydronium ions by adding hydroxyl ions but is necessary only to reduce its concentration by dilution, as in the case of bismuth trichloride, $BiCl_3$.

$$BiCl_3 + H_2O \rightarrow Bi(H_2O)_x^{+++} + 3Cl^-$$
$$Bi(H_2O)_x^{+++} + H_2O \rightarrow [Bi(OH)(H_2O)_{x-1}]^{++} + H_3O^+$$
$$[Bi(OH)(H_2O)_{x-1}]^{++} + H_2O \rightarrow [Bi(OH)_2(H_2O)_{x-2}]^{+} + H_3O^+$$
$$[Bi(OH)_2(H_2O)_{x-2}]^{+} + Cl^- \rightarrow [Bi(OH)_2Cl(H_2O)_y]^0$$
$$[Bi(OH)_2Cl(H_2O)_y]^0 \rightarrow \underset{\text{Bismuth oxychloride}}{BiOCl\downarrow} + zH_2O$$

Degree of Acidity or Basicity.—The second question that we must answer is how acidic or basic is the solution? In other words, what are the concentrations of hydronium and hydroxyl ions? We know that hydronium and hydroxyl ions will react to form water

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

but we can also ask, is the reverse reaction possible? The answer, of course, is that all reactions are reversible to some extent. The question then becomes, how reversible is the reaction, or what concentrations of hydronium ions and hydroxyl ions exist in equilibrium with pure water? To answer this, let us write the equilibrium constant for the reaction

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$k = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

and since the reaction goes forward only to a minute extent, the concentration of the water is practically unity, and the equilibrium, or ionization constant, as it is often called, becomes

$$K_w = [H_3O^+][OH^-]$$

The value of this constant has been determined experimentally at various temperatures. These values are shown in Table XVI. Since many calculations are carried out for room temperature, the value for 25° is commonly used, *i.e.*, 1.008×10^{-14}, or approximately 1×10^{-14}. Since the concentration of the hydronium ion is equal to the hydroxyl ion and since their product is equal to 1×10^{-14}, it is evident that the concentration of the hydronium ion (as well as the concentration of the hydroxyl ion) in pure water at 25° is the square root of 10^{-14} or 10^{-7}.

$$[H_3O^+][OH^-] =$$
$$[H_3O^+] = [OH^-] = 10^{-7}$$

TABLE XVI.—VARIATION OF IONIZATION CONSTANT OF WATER WITH TEMPERATURE
(H. S. Harned and W. J. Hamer, 1933)

Temperature, Degrees Centigrade	K_w
0	0.11×10^{-14}
10	0.29×10^{-14}
25	1.01×10^{-14}
40	2.92×10^{-14}
50	5.48×10^{-14}
100	$(56) \times 10^{-14}$

This symbol is often a little awkward to handle, and a simpler method of representing these facts has been devised. Let us take the common logarithm of both sides of this equation.

$$[H_3O^+] = 10^{-7}$$
$$\log [H_3O^+] = -7 \log 10$$

and since

$$\log 10 = 1$$
$$\log [H_3O^+] = -7$$

multiplying both sides by -1 gives

$$-\log [H_3O^+] = 7$$

Let us now replace the quantity $-\log [H_3O^+]$ by the symbol pH_3O or, more simply, pH. The equation becomes

$$pH = 7$$

That is, the pH of pure water at 25°C. is 7. If the pH of a solution is less than 7, the solution is acidic; if the pH is greater than 7, the solution is basic. Let us illustrate with a few examples.

Example 1.—The pH of a solution is 3. Is the solution acidic or basic?

$$pH = 3$$
$$-\log [H_3O^+] = 3$$
$$\log [H_3O^+] = -3 \log 10$$
$$[H_3O^+] = 10^{-3}$$

if

$$K_w = [H_3O^+][OH^-] = 10^{-14}$$
$$(10^{-3})[OH^-] = 10^{-14}$$
$$[OH^-] = \frac{10^{-14}}{10^{-3}}$$

Since 10^{-3} is greater than 10^{-11}, the hydronium ion is the predominant species, and the solution is acidic. In the preceding case

$$pOH = 11$$

i.e.

$$-\log [OH^-] = 11 = pOH$$

Example 2.—The pH of a solution is 9. Is the solution acidic or basic?

$$\begin{aligned} pH &= 9 = -\log [H_3O^+] \\ [H_3O^+] &= 10^{-9} \\ K_w &= \\ [OH^-] &= \frac{10^{-14}}{10^{-9}} = 10^{-5} \end{aligned}$$

10^{-9} is less than 10^{-5}; therefore the hydroxyl ion is predominant, and the solution is basic. The problem can be simplified by applying the laws of logarithms.

$$K_w = [H_3O^+][OH^-]$$

and taking the logarithms of both sides

$$\log K_w = \log [H_3O^+] + \log [OH^-]$$

or

$$-\log K_w = -\log [H_3O^+] - \log [OH^-]$$

since

$$\begin{aligned} -\log [H_3O^+] &= pH \\ -\log [OH^-] &= pOH \end{aligned}$$

and

$$\begin{aligned} -\log K_w &= pK_w \\ pK_w &= pH + pOH \end{aligned}$$

since

$$\begin{aligned} K_w &= 10^{-14} \\ -\log K_w &= 14 \log 10 = 14 = pK_w \end{aligned}$$

or

$$14 = pH + pOH$$

Hence if we have a solution of pH = 2, the pOH = 12; or if the solution has a pH = −1, the pOH = 15, etc. If the pH is less than pOH (in numerical value), the solution is acidic; if it is greater than the pOH, the solution is basic; and if the pH = pOH, the solution is neutral.

Let us now see how we can calculate the pH of a given solution. Let us take the cases that we have previously discussed on pages 109*ff*.

I. Neither the anion nor the cation reacts with water. The solution is neutral.

$$NaCl + xsH_2O \rightarrow Na(H_2O)_x^+ + Cl^-$$

Since no additional hydronium or hydroxyl ions are added to the solution by this reaction, the concentration of these ions in water remains undisturbed; *i.e.*

$$pH = pOH = 7$$

and the solution is neutral.

II. The anion but not the cation reacts with water. The solution will be basic.

$$NaCN + xsH_2O \rightarrow Na(H_2O)_x^+ + CN^-$$
$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$
$$K = \frac{[HCN][OH^-]}{[CN^-]}$$

From tables, it can be seen that the constant for the reaction

$$xsH_2O + HCN \rightleftharpoons H_3O^+ + CN^-$$

is

$$K' = \frac{[H_3O^+][CN^-]}{[HCN]} = 7.2 \times 10^{-10}$$

but since

$$K_w = [H_3O^+][OH^-]$$
$$[H_3O^+] = \frac{K_w}{[OH^-]}$$

Substituting, we obtain

$$K' = \frac{K_w[CN^-]}{[OH^-][HCN]}$$
$$K = \frac{K_w}{K'} = \frac{[OH^-][HCN]}{[CN^-]}$$
$$K = \frac{10^{-14}}{7.2 \times 10^{-10}}$$
$$K = 1.4 \times 10^{-5}$$

Now

$$K = 1.4 \times 10^{-5} = \frac{[HCN][OH^-]}{[CN^-]}$$

The concentration of the HCN is unknown but is equal to the concentration of OH^- and can therefore be represented by x. If the concentration of the cyanide ion originally placed in the solution was $0.01M$, the final concentration of CN^- is $(0.01 - x)$. Therefore

$$1.4 \times 10^{-5} = \frac{(x)(x)}{(0.01 - x)}$$

and

$$x^2 = (1.4 \times 10^{-7}) - (1.4 \times 10^{-5})x$$
$$x^2 + (1.4 \times 10^{-5})x - (1.4 \times 10^{-7}) = 0$$

This may be solved by the quadratic formula, giving

$$x = 3.67 \times 10^{-4} = [OH^-]$$
$$-\log [OH^-] = -\log 3.67 + 4 \log 10$$
$$pOH = -0.565 + 4 = 3.44$$
$$pH = 14 - 3.44 = 10.56$$

III. The cation but not the anion reacts with water. The solution is acidic.

$$0.01M \text{ solution of } NH_4Cl$$
$$NH_4Cl + xsH_2O \rightarrow NH_4^+ + Cl^- + xsH_2O$$
$$NH_4^+ + xsH_2O \rightleftharpoons NH_3 + H_3O^+ + xsH_2O$$
$$K = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

for the reaction

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$K' = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.75 \times 10^{-5}$$
$$\frac{K_w}{[H_3O^+]} = [OH^-]$$

Substituting

$$K' = \frac{[NH_4^+]}{[NH_3]} \cdot \frac{K_w}{[H_3O^+]}$$
$$K = \frac{K_w}{K'} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{10^{-14}}{(1.75 \times 10^{-5})}$$
$$K = 0.57 \times 10^{-9} = 5.7 \times 10^{-10}$$
$$K = 5.7 \times 10^{-10} = \frac{(x)(x)}{(0.01 - x)}$$
$$(5.7 \times 10^{-12}) - (5.7 \times 10^{-10})(x) = x^2$$
$$x^2 + (5.7 \times 10^{-10})(x) - (5.7 \times 10^{-12}) = 0$$
$$x = (2.4 \times 10^{-6}) = [H_3O^+]$$
$$-\log [H_3O^-] = -\log 2.4 + 6 \log 10$$
$$pH = -0.38 + 6 = 5.62$$

IV. If both the cation and the anion react with water, the solution may be acidic, basic, or neutral.

Example 1.—$0.01M$ solution of ammonium acetate.

$$NH_4C_2H_3O_2 + xsH_2O \rightarrow NH_4^+ + C_2H_3O_2^- + xsH_2O$$
$$NH_4^+ + xsH_2O \rightleftharpoons NH_3 + H_3O^+ + xsH_2O$$
$$K_{\text{cation}} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.7 \times 10^{-10}$$
$$C_2H_3O_2^- + xsH_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$
$$K_{\text{anion}} = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = 5.6 \times 10^{-10}$$
$$K_{\text{cation}} = \frac{(x)(x)}{(0.01 - x)} = 5.7 \times 10^{-10}$$

Since x is so small

$$0.01 - x = \text{approximately } 0.01$$
$$x^2 = 5.7 \times 10^{-12}$$

$$x = [H_3O^+] = 2.38 \times 10^{-6}$$

$$K_{\text{anion}} = \frac{(y)(y)}{(0.01 - y)} = 5.6 \times 10^{-10}$$

Similarly, since y is small

$$(0.01 - y) = 0.01$$

$$y^2 = 5.6 \times 10^{-12}$$

$$y = [OH^-] = 2.4 \times 10^{-6}$$

and since the concentration of OH^- is equal (approximately) to the concentration of the H_3O^+, the solution is neutral.

Example 2.—0.01M ammonium hypochlorite.

$$NH_4ClO + xsH_2O \rightarrow NH_4^+ + ClO^-$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$K_{\text{cation}} = \frac{[H_3O^+][NH_3]}{[NH_4^+]} = 5.7 \times 10^{-10}$$

$$K_{\text{cation}} = \frac{(x)(x)}{(0.01 - x)} = 5.7 \times 10^{-10}$$

$$x^2 = 5.7 \times 10^{-12}$$

$$x = [H_3O^+] = 2.38 \times 10^{-6}$$

$$ClO^- + H_2O \rightleftharpoons HClO + OH^-$$

$$K_{\text{anion}} = \frac{[OH^-][HClO]}{[ClO^-]} = 2.7 \times 10^{-7}$$

$$K_{\text{anion}} = \frac{(y)(y)}{(0.01 - y)} = 27.0 \times 10^{-8}$$

$$y^2 = 27.0 \times 10^{-10}$$

$$[OH^-] = y = 5.19 \times 10^{-5}$$

Recapitulating

$$[OH^-] = 5.19 \times 10^{-5} = 51.9 \times 10^{-6}$$

$$[H_3O^+] = 2.38 \times 10^{-6}$$

Since they will neutralize one another, the final $[OH^-]$ will be

$$[OH^-] - [H_3O^+] = (51.9 \times 10^{-6}) - (2.38 \times 10^{-6})$$

$$[OH^-] = 49.52 \times 10^{-6} = 4.95 \times 10^{-5}$$

$$pOH = -\log [OH^-] = -\log 4.95 + 5 \log 10$$

$$pOH = -0.69 + 5 = 4.31$$

$$pH = 9.69$$

The solution is basic.

Conclusions.—Unfortunately, these methods of calculation have their limitations. (1) They apply only to very dilute solutions, *i.e.*, solutions in which the molecules are widely separated by solvent molecules. (2) They do not apply to all substances that give acidic or basic solutions; they apply only to solutions in which the hydronium

ion concentration is relatively low. If the hydronium ion concentration is high, other effects enter that complicate the picture immensely. (3) The calculations made here use the actual concentrations, whereas a quantity called the activity should be used. The activity is the effective concentration of the ion in question, *i.e.*, the concentration that it appears to possess. The activity is an empirical factor that is determined experimentally. In very dilute solutions, the activity and the concentration approach equality; hence the usefulness of these calculations when applied to such solutions.

READING REFERENCES

LUDER, W. FAY: The Electronic Theory of Acids and Bases, *Chem. Rev.*, Vol. 27, December, 1940.

SMITH, G. B. L.: Selenium Oxychloride as a Solvent, *Chem. Rev.*, Vol. 23, August, 1938.

Symposium on Acids and Bases, *J. Chem. Education*, Mack Printing Company, Easton, Pa.

QUESTIONS

1. How many grams of lead acetate are needed to prepare a liter of $1.62M$ solution, A $1.62N$ solution?

2. What is the molality of a 3.10 mole per cent solution of cadmium chloride? What is the weight per cent composition?

3. How many milliliters of H_2SO_4 sp. gr. $\frac{20°}{4°} = 1.855$ are needed to prepare 125 ml. of a $0.75N$ solution? What is the molarity of this solution?

4. What is the normality of 99% sulfuric acid? 36% HCl? 70% HNO_3?

5. What is the normality of a 12% solution of K_2CrO_4 relative to potassium? To chromate ion?

6. What mole fractions of H_2O and $BeSO_4$ are present in a 7.20 molal solution of $BeSO_4 \cdot 4H_2O$?

7. Given a 22.4% solution of microcosmic salt, what is the mole fraction of each ion and compound present?

8. A $0.5M$ solution of $K_2Cr_2O_7$ is of what normality?

9. The solvo-ions in solutions of liquid sulfur dioxide are SO^{--} and SO_3^{++}. Thionyl chloride, $SOCl_2$, gives a basic solution in this solvent, and potassium sulfite gives an acidic solution. Write reactions for the solution of these substances in SO_2, and write the neutralization reaction.

10. What is the pH of a solution that has a $[H_3O^+] = 2.35 \times 10^{-8}$? Is the solution acidic or basic?

11. What are the $[H_3O^+]$ and $[OH^-]$ in solutions having the following pH: 7.32, 3.42, 1.01, −3.25, 11.2, 18, 0, 14?

12. What is the pH of an $0.012M$ solution of ammonium sulfate?

13. What is the pOH of an $0.011M$ solution of sodium azide? Is the solution acidic or basic?

14. What is the pH of an $0.05M$ solution of NH_4Cl? Of an $0.005M$ solution? Of an $0.0005M$ solution?

15. What sort of solution do you predict that the following will give in liquid NH_3: KCl, KNH_2, $(NH_4)_2SO_4$, NH_4NO_3, Li, SO_3? Write the reactions.

CHAPTER VIII

REACTIONS OF CHEMICAL COMPOUNDS

III. REACTIONS IN SOLUTION

The ability of the chemist to predict the outcome of future experiments is very likely to impress the outsider as a faculty bordering on the supernatural. In reality, as Sherlock Holmes would have assured his friend Dr. Watson, "It is all very elementary" (once you know how it is done). The most dramatic example is, of course, that of Mendelejeff predicting the discovery of a then unknown element and describing it in minute detail as if he had had a sample of it at hand. We shal. study somewhat less spectacular examples of chemical forecasting. These more prosaic cases are nevertheless the backbone of the chemists' work.

Mass-action Law.—One of the important things that the chemist would like to be able to predict is the effect of the addition of one solution to another. Sometimes this is possible; many times it is impossible. Many exact predictions are based upon certain principles, one of which is the mass-action law. In Chap. VI, we considered the formation and decomposition of hydrogen iodide. In this case, we saw that an equilibrium constant could be written for the reaction

$$2HI \rightleftharpoons H_2 + I_2$$

$$K = \frac{C_{H_2} \times C_{I_2}}{C_{H}}$$

This particular equilibrium constant remains essentially constant for any definite temperature. Hence we could calculate the concentration of HI that would result from the interaction of varying proportions of H_2 and I_2. This principle can be extended to the case of solutions. If we have two substances, A and B, in solution, which react to form C and D

we can express the equilibrium constant thus:

$$K = \frac{C_C \times C_D}{\times}$$

If into this system we introduce more of D, the quantities of the various

components present will change so that the equilibrium constant remains fixed; *i.e.*, the addition of C or D will result in the formation of more A and B and vice versa. This principle is termed the mass-action law. In a great many cases, the extent of the reaction of C and D to form A and B is much smaller than the opposing reaction. Hence the forward reaction may go practically to completion. There are several reasons why a reaction goes practically to completion. These will be considered separately.

CASE I. DIFFICULTLY SOLUBLE PRECIPITATE AS A REACTION PRODUCT

We shall choose as our first example the familiar test for barium that consists of the addition of a soluble sulfate to a solution containing barium ion to form a white precipitate of barium sulfate. We must now take into account the equilibrium between the solid substance $BaSO_4$ and its solution. This equilibrium can be referred to as a "heterogenous equilibrium," or "complex equilibrium," as some authors prefer to call it. Barium sulfate is soluble in water at 25°C. to the extent of about 2.5 mg. per liter of solution or 1 part in 400,000 parts of water by weight. Barium sulfate is, of course, a strong electrolyte. A saturated solution is so dilute that we may assume that the activity coefficient of the ions is unity. In applying the mass-action law to the equilibrium, we must remember that we are concerned with an equilibrium of the solid barium sulfate, with a solution of its ions:

$$BaSO_{4_{solid}} \xrightleftharpoons{xsH_2O} Ba^{++} + SO_4^{=}$$

$$K_c = \frac{C_{Ba^{++}} \times C_{SO_4^{=}}}{C_{BaSO_4}} \qquad \text{or} \qquad \frac{[B}{[}$$

Since the activity of a solid is constant, then

$$K_{sp} = [Ba^{++}][SO_4^{=}] = K_c[BaSO_4]$$

The new constant is termed the solubility product constant.

Let us consider another example, a saturated solution of lead chloride. Each molecule of lead chloride yields, on solution, one lead ion and two chloride ions, but we may write the reaction in a stepwise fashion thus:

$$PbCl_{2_{solid}} \xrightleftharpoons{xsH_2O} PbCl^{+} + Cl^{-} \tag{1}$$

and

$$PbCl^{+} \xrightleftharpoons{xsH_2O} Pb^{++} + Cl^{-} \tag{2}$$

The equilibrium expression for reaction (1) is

$$K_1 =$$

and for reaction (2) is

$$K_2 = \frac{[Pb^{++}][Cl^-]}{[PbCl^+]}$$

Multiplying the first by the second, we get

$$K_e = K_1 \times K_2 =$$

or

$$K_e = \frac{\quad}{[PbCl_2]}$$

Since the same reasoning applies in this case as in the case of a saturated solution of barium sulfate, it follows that

$$K_{sp} = [Pb^{++}][Cl^-]^2$$

Definition of the Solubility-product Principle.—We may now summarize the solubility-product principle. **In the case of a saturated**

TABLE XVII.—SOLUBILITY-PRODUCT CONSTANTS

$PbCl_2$	1×10^{-4}	(25°C.)
$AgCl$	1.1×10^{-10}	(20°C.)
Hg_2Cl_2	2×10^{-18}	(25°C.)
HgS	3×10^{-53}	
PbS	1×10^{-29}	
CuS	4.0×10^{-38}	
CdS	3.6×10^{-29}	(18°C.)
SnS	8.0×10^{-29}	
NiS	1.4×10^{-24}	(18°C.)
CoS	3.0×10^{-26}	(18°C.)
FeS	3.7×10^{-19}	(18°C.)
MnS	1.4×10^{-15}	(18°C.)
ZnS	1.2×10^{-23}	(18°C.)
$Al(OH)_3$	1.9×10^{-33}	
$Cr(OH)_3$	6.7×10^{-31}	
$BaCrO_4$	2.0×10^{-10}	(25°C.)
$SrSO_4$	2.8×10^{-7}	(17°C.)
CaC_2O_4	2.3×10^{-9}	
$MgNH_4PO_4$	2.5×10^{-13}	(25°C.)
$PbCrO_4$	1.8×10^{-14}	(18°C.)
Ag_2CrO_4	9×10^{-12}	(25°C.)
$Fe(OH)_3$	4×10^{-38}	
$Mg(OH)_2$	1.46×10^{-11}	(18°C.)
Bi_2S_3	5.68×10^{-31}	(18°C.)
$BaSO_4$	1×10^{-10}	(25°C.)
AgI	8.5×10^{-17}	

solution of a difficultly or sparingly soluble electrolyte, the product of the concentration of the constituent ions is sensibly constant at any given

temperature. As can be seen from the latter example, if two of the ions produced are alike, the concentration of the ion is squared. In general, therefore, the concentration of each ion is raised to a power that is equal to the number of ions produced. Although this definition of the solubility-product principle seems ironclad, it is based upon an assumption, *i.e.*, that the activity is equal to the concentration. Since in very dilute solutions, such as occur in the case of difficulty soluble substances, this is approximately true, we can use the solubility-product principle profitably.

Calculation of the Solubility Product

Example 1.—Let us assume that we want to determine the K_{sp} for AgCl, the difficulty soluble silver compound that enables the chemist to isolate silver from a mixture. First of all, we should have to determine how much silver chloride dissolves in 1 liter of water. This would be found to be 0.0015 gram per liter at room temperature (20°C.). To transpose this quantity into molar concentrations, we divide 0.0015 by the molecular weight of AgCl, namely, 143.34, and $\frac{0.0015}{143.34} = 1.05 \times 10^{-5}$. Since we assume that all the AgCl is dissociated into Ag^+ and Cl^-, the concentration of Ag^+ would be 1.05×10^{-5}, and that of Cl^- would be 1.05×10^{-5}. Substituting these values in the equation

$$K_{sp} = [Ag^+][Cl^-]$$

and

$$K_{sp} = (1.05 \times 10^{-5})(1.05 \times 10^{-5})$$
$$K_{sp} = 1.1 \times 10^{-10}$$

Example 2.—Magnesium hydroxide is soluble to the extent of 0.0009 gram per 100 grams of water at 18°C. What is the solubility product of this compound? Since the volume occupied by 0.0009 gram of $Mg(OH)_2$ is small compared with the volume occupied by the 100 grams of water, we may assume that the total volume is equal to the volume of the water, namely, 100 ml. Hence the molar concentration of $Mg(OH)_2$ is equal to

$$0.009 \text{ g./liter}$$

The molecular weight of $Mg(OH)_2 = 58.33$

$$\frac{0.009}{58.33} = 0.000154 \text{ mole/liter of } Mg(OH)_2$$

$$\text{The concentration of } Mg^{++} = 0.000154M = 1.54 \times 10^{-4}$$
$$\text{The concentration of } OH^- = 2 \times 1.54 \times 10^{-4} = 3.08 \times 10^{-4}$$
$$K_{sp} = [Mg^{++}][OH^-]^2 = (1.54 \times 10^{-4})(3.08 \times 10^{-4})^2 = 1.46 \times 10^{-11}$$

Example 3.—0.000018 gram of Bi_2S_3 dissolves in 100 grams of H_2O at 18°C. What is its K_{sp}?

$$0.000018 \text{ g.}/100 \text{ g.} \approx 0.00018 \text{ g./liter}$$

$$\frac{0.00018 \text{ g.}}{514.2} = 0.00000035M = 3.5 \times 10^{-7}$$

$$C_{Bi^{+++}} = 2 \times 3.5 \times 10^{-7} = 7.0 \times 10^{-7}$$

$$C_{S^{=}} = 3 \times 3.5 \times 10^{-7} = 1.05 \times 10^{-6}$$

$$\begin{aligned} K_{sp} &= [Bi^{+++}]^2[S^{=}]^3 = (7.0 \times 10^{-7})^2(1.05 \times 10^{-6})^3 \\ &= (49.0 \times 10^{-14})(1.16 \times 10^{-18}) \\ &= 5.68 \times 10^{-31} \end{aligned}$$

Example 4.—The K_{sp} of Ag_2CrO_4 at 25° is 9×10^{-12}. What is the molarity of this solution, and what is the solubility of Ag_2CrO_4?

$$K_{sp} = [Ag^+]^2[CrO_4^{=}] = 9 \times 10^{-12}$$

Let the number of moles of Ag_2CrO_4 present be represented by x. The concentration of $Ag^+ = 2x$.

$$\begin{aligned} (2x)^2(x) &= 9 \times 10^{-12} \\ 4x^3 &= 9 \times 10^{-12} \\ x^3 &= 2.25 \times 10^{-12} \\ x &= \sqrt[3]{2.25} \times 10^{-4} \\ x &= 1.3 \times 10^{-4} = \text{molarity of } Ag_2CrO_4 \end{aligned}$$

$$\text{Molecular weight of } Ag_2CrO_4 = 332$$

$$332 \times 0.00013 = 0.043 \text{ g./liter} = 0.0043 \text{ g./100 ml.}$$

Application of the Solubility-product Principle.—We now intend to show how this principle enables us to predict the course of a reaction, in which a difficultly or sparingly soluble precipitate appears as a reaction product. Let us suppose that we are interested in determining the $[SO_4^{=}]$ content of a solution. Could we precipitate the sulfate as $BaSO_4$ and then weigh it? To put it differently, does the reaction

$$- SO_4^{=} \rightleftharpoons BaSO_4$$

go sensibly to completion from left to right? In order to answer this question, we must know that the K_{sp} for $BaSO_4$ is 1×10^{-10}. In a saturated aqueous solution of barium sulfate, the concentration of the constituent ions is, therefore, 1×10^{-5} gram mole per liter of solution. We may compute from this the concentration of the respective substances in terms of grams per liter.

$$= 1 \times 10^{-5} \times 137.36 = 0.0013736 \text{ g./liter}$$

$$_4^{=}] = 1 \times 10^{-5} \times 96.07 = 0.0009607 \text{ g./liter}$$

$$[BaSO_4] = 1 \times 10^{-5} \times 233.43 = 0.0023343 \text{ g./liter}$$

Hence the solubility of barium sulfate in aqueous solution is appreciable. If we precipitate from a volume of 250 ml. and use 150 ml. of water to wash the precipitate, we have used sufficient water to dissolve approximately 1 mg. of barium sulfate. Of course, in actual practice, it is customary and necessary to use a slight excess of reagent (in our case, $BaCl_2$) in order to be certain that we have a stoichiometric quantity present and also to reduce the solubility of barium sulfate. If 250 ml. of solution has been employed, to which has been added sufficient barium chloride so that the final concentration of barium ions is $0.001M$ (this requires only about 0.5 ml. excess of a 10 per cent solution of barium chloride), then

$$[Ba^{++}][SO_4^{=}] = 1 \times 10^{-10}$$

and

$$[SO_4^{=}] = \frac{1 \times 10^{-10}}{1 \times 10^{-3}} = 1 \times 10^{-7}$$

and the concentration of sulfate ion remaining in solution will be

$$10^{-7} \times 96.07 = 0.000009607 \text{ g./liter}$$

and that of barium sulfate is

$$10^{-7} \times 233.43 = 0.000023343 \text{ g./liter}$$

The solubility of barium sulfate has been thus reduced to less than 0.01 mg. in 250 ml. of solution. For the reason illustrated, it is invariably the practice in analytical chemistry to effect precipitations by adding a slight but distinct excess of reagent.

CASE II. DILUTE ACETIC ACID AND SODIUM ACETATE; COMMON ION EFFECT AND BUFFER SOLUTIONS

We shall start with the experimental fact that a dilute acetic acid solution is found to be weakly acidic. (A careful rereading of Chap. VII should make this apparently blatant truism somewhat less obvious.) This can be explained by pointing out that the reaction between hydrogen acetate and water is incomplete and reaches equilibrium when the hydronium ion concentration is still relatively small.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Written in the mass action equation, the reaction becomes

$$K_e = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

In a $1M$ acetic acid solution the concentration of unchanged hydrogen acetate is 0.9958 moles. The concentration of the hydronium and

acetate ions is therefore 0.0042 moles each. Substituting these values in the equation, we can calculate the equilibrium constant

$$\frac{(0.0042)(0.0042)}{(0.9958)} = 1.8 \times 10^{-5}$$

It stands to reason that this constant should remain unchanged irrespective of changes in the concentrations of the components.

We now propose to perform a rather instructive experiment; let us drastically increase the acetate ion concentration by adding a sodium acetate solution. By using the equilibrium equation, we can predict that since K remains unchanged, increasing the concentration of one of the ions in the numerator should considerably decrease the concentration of the other ion and also increase the denominator. To verify this contention experimentally, let us add 1 mole of sodium acetate to the foregoing acetic acid solution. Molar sodium acetate, according to Arrhenius, would have been declared to be 53 per cent ionized. We have become, however, more cautious about such things, and we shall merely admit that the effective available concentration of acetate ion is 0.53 mole. Incorporating this value in the equation, we find that

$$\frac{(0.0042 - x)(0.5342 - x)}{8 + x} = 1.8 \times 10^{-5}$$

where x moles of acetate ion combine with x moles of hydronium ion to form x moles of acetic acid. Hence

$$\begin{aligned}(0.5342 - x) &= [CH_3COO^-] \text{ remaining}\\ (0.0042 - x) &= [H_3O^+] \text{ remaining}\\ (0.9958 + x) &= [CH_3COOH] \text{ after addition}\end{aligned}$$

Expanding and solving for x, we get

$$x = 0.004167$$

or

$$\begin{aligned}[H_3O^+] &= 0.000033 \text{ mole/liter}\\ [CH_3COO^-] &= 0.530033\\ [CH_3COOH] &= 0.999467\end{aligned}$$

Thus the experiment has verified our prediction. But does it have any practical value? This can be answered by pointing out that it constitutes a procedure generally designated as "the common ion effect," which is of utmost importance in analytical operations. To cite only two outstanding examples, the separation of Group II from Group III in cation analysis is based on this principle. (For a discussion of this case, see page 129). As our second example, we shall consider the

prevention of the precipitation of magnesium hydroxide in the third group. In this group, certain hydroxides, namely, those of iron, chromium, and aluminum, are prec pitated by the addition of ammonium hydroxide. If the solution contained magnesium ion, it would also be precipitated by the simple addition of ammonium hydroxide. To prevent this, we make use of the common ion effect. The solubility product of

$$Fe(OH)_3 = 4 \times 10^{-38}$$
$$Al(OH)_3 = 1.9 \times 10^{-33}$$
$$Cr(OH)_3 = 6.7 \times 10^{-33}$$

whereas, on the other hand, the solubility product of magnesium hydroxide is

$$Mg(OH)_2 = 1.46 \times 10^{-11}$$

Hence, if we could find a method of decreasing the hydroxyl ion concentration, we could prevent the precipitation of magnesium hydroxide. If we add ammonium chloride, the increase in the ammonium ion concentration will sufficiently lower the hydroxyl ion concentration and thus prevent the precipitation of magnesium hydroxide.

Buffer Solutions.—Let us refer again to the equilibrium equation of dilute acetic acid.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{\quad} = 1.8 \times 10^{-5}$$

Assume now that we make the concentration of acetate ion equal to that of hydrogen acetate. Then

$$= 1.8 \times 10^{-5}$$

It can be seen that the concentration of the hydronium ion has become equal to that of the equilibrium constant 1.8×10^{-5}. The implicaions are quite apparent. In numerous chemical and, more particularly, biochemical processes, it is imperative to maintain a definite hydronium ion concentration fixed within narrow limits. Numerous microorganisms, for instance, refuse to grow unless the $[H_3O^+]$ is adjusted to a certain level. Solutions of the sodium acetate-hydrogen acetate type are therefore widely used. They are called buffer solutions and are prepared by selecting appropriate concentrations of weak acids in equilibrium with the corresponding anions. Two hundred milliliters of a solution containing 50 ml. of 0.2*M* primary potassium phthalate and 0.4 ml. of 0.2*M* NaOH will maintain a hydronium ion concentration of 10^{-4} or a pH of 4.

The name buffer is quite appropriately chosen. If we refer once more to the acetic acid equilibrium, it can readily be shown that the presence of a larger amount of sodium acetate would resist and minimize the accidental introduction of some strong acid, and that the reaction

$$H_3O^+ + (C_2H_3O_2)^- \rightarrow HC_2H_3O_2$$

would take place and thus maintain the original H_3O^+ ion concentration. This mechanism is vital to us in the most literal sense of the word. Human blood must maintain a H_3O^+ concentration corresponding to a pH of 7.6. Any deviation from this level would lead to serious, perhaps fatal, injury. Blood is therefore protected by the presence of such buffers as bicarbonates, phosphates, etc.

CASE III. FORMATION OF SLIGHTLY IONIZED PRODUCT

When we deal with difficultly soluble salts of weak acids, it is possible to regulate the hydronium ion concentration of the solution so as to control with very high precision the concentration of the anions of the weak acids. This is, in brief, the principle upon which is based the separation of the metal sulfides of the hydrogen sulfide group from the ammonium sulfide group in the ordinary qualitative scheme.

Separation of the Cations of Group II from Those of Group III.—By purely empirical methods, the pioneers of analytical chemistry had found that, whenever a solution containing the ions of Groups II and III was made $0.3N$ with hydrochloric acid and saturated with hydrogen sulfide, only the sulfides of Group II, *i.e.*, cupric sulfide, bismuth sulfide, arsenic sulfide, etc., would precipitate. The other ions present were left in solution. This method of separation has proved to be so convenient that it is retained in practically all the analytical schemes. Careful experiments have shown that this separation is definitely dependent upon the hydronium ion concentration. If the analyst should become careless and try to precipitate the sulfides from a solution of greater acidity (*e.g.*, one that is $3N$), he would find that a number of the cations of the second group, *e.g.*, Cd^{++}, Sn^{++}, Pb^{++}, Bi^{+++}, would not form any insoluble sulfides. On the other hand, a solution only $0.02N$ with respect to the hydronium ion would allow the precipitation of zinc sulfide, which is a member of Group III.

Let us now show how all these experimental facts can be accurately predicted with the help of the common ion principle and a chemical handbook. The reaction of H_2S with water can be represented by the following equations:

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$$
$$HS^- + H_2O \rightleftharpoons H_3O^+ + S^=$$

Hence the equilibrium constant for these reactions would be formulated thus:

$$K_1 = \frac{C_{H_3O^+} \times C_{HS^-}}{C_{H_2S}}$$

and

$$K_2 = \frac{C_{H_3O^+} \times C_{S^=}}{C_{HS^-}}$$

Multiplying K_1 by K_2, we get

$$K = K_1K_2 = \frac{(C_{H_3O^+})^2 \times C_{S^=}}{C_{H_2S}}$$

At room temperature (25°C.) and 1 atm. pressure, a liter of water saturated with hydrogen sulfide contains 0.1 mole of H_2S.
In this solution the

$$\begin{aligned} H_3O^+ \text{ concentration} &= 9.5 \times 10^{-5} \\ HS^- \text{ concentration} &= 9.5 \times 10^{-5} \\ S^= \text{ concentration} &= 1.2 \times 10^{-15} \end{aligned}$$

Substituting these values in the expressions for the equilibrium constants, we obtain

$$K_1 = \frac{(9.5 \times 10^{-5})(9.5 \times 10^{-5})}{0.1} = 9 \times 10^{-8}$$

$$K_2 = \frac{(9.5 \times 10^{-5})(1.2 \times 10^{-15})}{(9.5 \times 10^{-5})} = 1.2 \times 10^{-15}$$

$$K = K_1K_2 = (9 \times 10^{-8})(1.2 \times 10^{-15}) = 1.1 \times 10^{-22}$$

We have thus calculated the equilibrium constant for a saturated solution of hydrogen sulfide. We can now write the equilibrium expression in this form:

$$(C_{H_3O^+})^2 \times C_{S^=} = (1.1 \times 10^{-22})(0.1) = 1.1 \times 10^{-23}$$

and

$$C_{S^=} = \frac{(1.1 \times 10^{-23})}{(C_{H_3O^+})^2}$$

This equation shows obviously what the relation is between the hydronium ion concentration and the sulfide ion concentration. The sulfide ion concentration is inversely proportional to the square of the hydronium ion concentration. A tenfold increase in the hydronium ion concentration decreases the sulfide ion concentration a hundredfold.

Let us now show how some simple calculations would permit us to predict that, if a solution containing cadmium ion and zinc ion is made

0.3N with hydrochloric acid and then saturated with hydrogen sulfide, only cadmium would precipitate as the sulfide. Let us use the equation obtained above and substitute 0.3 for the hydronium ion concentration (the amount of H_3O^+ formed by the dissociation of the H_2S is so small that it may be neglected) and thus calculate the concentration of the sulfide ion in this solution.

$$C_{S^=} = \frac{(1.1 \times 10^{-23})}{(0.3)^2} = \frac{(1.1 \times 10^{-23})}{0.09}$$
$$C_{S^=} = 1.2 \times 10^{-22}$$

Let us assume that the solution that we wish to test is 0.01M with respect to cadmium ion and 0.01M with respect to zinc ion. The solubility products of the corresponding sulfides are

$$\text{CdS},\ K_{sp} = 3.6 \times 10^{-29}$$
$$\text{ZnS},\ K_{sp} = 1.2 \times 10^{-23}$$

Substituting the values obtained previously, we have

$$\text{ZnS},\ K = [Zn^{++}][S^=] = (1.1 \times 10^{-22})(0.01)$$
$$K = 1.1 \times 10^{-24}$$

Since $K_{sp} > K$, zinc sulfide would not precipitate; *i.e.*, the product of the sulfide ion concentration and the zinc ion concentration is smaller than the value of solubility product. On the other hand, for cadmium sulfide, we have

$$K = [Cd^{++}][S^=] = (1.1 \times 10^{-22})(0.01)$$
$$K = 1.1 \times 10^{-24}$$

Since here $K > K_{sp}$, cadmium sulfide would precipitate.

We may also compute the concentration of the cadmium ion remaining in solution after the reaction has reached equilibrium.

$$[Cd^{++}][S^=] = 3.6 \times 10^{-29}$$
$$[Cd^{++}](1.1 \times 10^{-22}) = 3.6 \times 10^{-29}$$
$$[Cd^{++}] = \frac{3.6 \times 10^{-29}}{1.1 \times 10^{-22}} = 3.3 \times 10^{-7}$$
$$[Cd^{++}] = 0.00000033 \text{ mole/liter}$$

This fact, expressed in words, plainly indicates that the amount of cadmium ion remaining in solution is negligible. We have selected one representative ion in both the hydrogen sulfide group and the ammonium sulfide group. We should like to suggest to the student who possesses both a healthy curiosity and an appropriate amount of skepticism that he test the general principle illustrated above by calculating the ion products for the other members of Group II and of

Group III and compare them with the solubility products of the corresponding sulfides.

CASE IV. FORMATION OF A VOLATILE GAS

Let us assume that a solution containing Ba^{++} has been treated with $(NH_4)_2CO_3$ solution, thus forming a precipitate of white, powdery $BaCO_3$. This is a procedure commonly resorted to in qualitative analysis to isolate the alkaline-earth group. Barium carbonate is the salt of a moderately strong base and a weak acid. Its solubility product could be written as

$$[Ba^{++}][CO_3^{=}] = 8.1 \times 10^{-9}$$

from the equation

$$BaCO_{3_{solid}} \rightleftharpoons Ba^{++} + CO_3^{=}$$

If, to a saturated aqueous solution of barium carbonate in contact with solid barium carbonate, we add a small amount of a strong acid (let us say hydrochloric acid), there will be a reaction with the carbonate ions, resulting in the formation of carbonic acid, which will further break up into CO_2 and H_2O.

$$CO_3^{=} + H_3O^+ \rightarrow HCO_3^- + H_2O$$
$$HCO_3^- + H_3O^+ \rightarrow H_2CO_3 \rightarrow H_2O + CO_2 \uparrow$$

In this way, the concentration of the carbonate ion will be reduced, and the equilibrium will be displaced to the right. In other words, barium carbonate will dissolve in an attempt to maintain an ion concentration sufficient to satisfy the solubility product. Under the same circumstances, barium sulfate would not dissolve, because the presence of a nonvolatile acid would not materially affect the concentration of the sulfate ion. In the same way, a salt of a volatile base and a strong acid may be dissolved by the addition of a solution of a strong base to its saturated solution in contact with the solid salt.

CASE V. FORMATION OF A COMPLEX ION

The fact that silver chloride is soluble in a solution of ammonia is applied to the separation of the metals of the first group. It is cited here to illustrate the relationship between solubility product and complex ion formation. If we have a saturated solution of silver chloride in contact with solid silver chloride and add ammonia solution, the silver chloride will dissolve if enough ammonia has been added.

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$
$$Ag^+ + 2NH_3 \rightarrow Ag(NH_3)_2^+$$

However, the diamminosilver ion dissociates to a certain extent:

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$$

The equilibrium constant for this reaction is

$$K = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6.8 \times 10^{-8}$$

In order to examine the effect of an ammonia solution on the equilibrium between Ag^+ and Cl^- and solid AgCl, let us assume the following conditions: a solution of silver nitrate whose total $[Ag^+]$ is $0.01M$ has been treated with NH_3 solution until the concentration of the latter is $0.1M$. We now ask the question, what is the concentration of free $[Ag^+]$ remaining in this solution? Utilizing the equilibrium expression

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6.8 \times 10^{-8}$$

we can readily find the answer if we incorporate the following known concentrations into the formula. Since the original silver ion concentration is $0.01M$ and since $Ag(NH_3)_2^+$ is only slightly dissociated, we may assume that

$$[Ag(NH_3)_2^+] = 0.01M$$

The $[NH_3]$ is 0.1; therefore $[NH_3]^2 = 0.01$. Incorporating these values in the equilibrium expression, we have

$$\frac{[Ag^+] \times (0.01)}{(0.01)} = 6.8 \times 10^{-8}$$

from which follows that the $[Ag^+] = 6.8 \times 10^{-8}$. In other words, under the stipulated conditions and after the formation of the silver ammonia complex, 6.8×10^{-8} mole of Ag^+ remains in solution. Let us now investigate this system further in order to determine the chloride ion concentration required to cause a precipitate of AgCl. The solubility product of AgCl is 1.1×10^{-10}. Let us now calculate the $[Cl^-]$ that must be exceeded in order to cause precipitation.

$$K_{sp} = [Cl^-][Ag^+] = 1.1 \times 10^{-10}$$
$$[Cl^-](6.8 \times 10^{-8}) = 1.1 \times 10^{-10}$$
$$[Cl^-] = \frac{1.1 \times 10^{-10}}{6.8 \times 10^{-8}} = 1.62 \times 10^{-3}$$

In the absence of ammonia solution and the same total concentration of silver ion as silver nitrate ($0.01M$), precipitation would have resulted when the chloride ion concentration exceeded 1.1×10^{-8}.

One interesting observation is that whereas silver chloride is soluble in an ammonia solution, silver iodide is insoluble in ammonia. This fact can be explained on the basis of the solubility product of silver iodide.

$$K_{sp} = 8.5 \times 10^{-17}$$

That is, a saturated solution of silver iodide contains the following silver ion concentration:

$$[Ag^+][I^-] = 8.5 \times 10^{-17}$$

since $[Ag^+] = [I^-]$

$$[Ag^+]^2 = 85 \times 10^{-18}$$
$$[Ag^+] = 9.2 \times 10^{-9}$$

But the concentration of silver ion furnished by the dissociation of the diamminosilver complex is 6.8×10^{-8}. This means that since the dissociation of the diamminosilver ion furnishes more silver than is necessary for silver iodide to precipitate, adding iodide ion to a solution of silver chloride in ammonia would result in the precipitation of silver iodide.

K, the constant that governs the equilibrium between the complex ion and its components, is customarily designated as the **instability constant.** The justification for this term can be readily realized when we consider that the smaller the instability constant the smaller the concentration of free ions in equilibrium with the complex ion.

Another important application of this principle is found in the separation of cyanides of copper and cadmium by means of hydrogen sulfide. The equilibrium constants for the dissociation of these complex cyanides are

$$Cu(CN)_3^{=} \rightleftharpoons Cu^+ + 3CN^-$$
$$K_{\text{instability}} = \frac{[Cu^+][CN^-]^3}{[Cu(CN)_3^{=}]} = 5 \times 10^{-28}$$
$$Cd(CN)_4^{=} \rightleftharpoons Cd^{++} + 4CN^-$$
$$K_{\text{instability}} = \frac{[Cd^{++}][CN^-]^4}{[Cd(CN)_4^{=}]} = 1.4 \times 10^{-17}$$

We can see that the instability constant for cadmium is considerably greater than that for copper. When hydrogen sulfide is introduced, the sulfide ion concentration is great enough to exceed the solubility product of the cadmium sulfide but not great enough to exceed that of the cuprous sulfide. Hence this is a commonly used separation procedure.

READING REFERENCES

GETMAN, F. H., and F. DANIELS: "Outlines of Theoretical Chemistry," 6th ed., John Wiley & Sons, Inc., New York, 1937.

GLASSTONE, S.: "Textbook of Physical Chemistry," D. Van Nostrand Company, Inc., New York, 1940.

HAMMETT, L. P.: "Solutions of Electrolytes," 2d ed., McGraw-Hill Book Company, Inc., New York, 1936.

QUESTIONS

1. The solubility of AgCl at 100°C. is 0.002 g./100 g. of water. Calculate the solubility-product constant.

2. The solubility of Hg_2Cl_2 at 40°C. is 0.0007 g./100 g. of water. Compute the solubility-product constant.

3. At 20°C., the solubility of $Ag_3Fe(CN)_6$ is 6.6×10^{-5} g./100 g. of water. Calculate the solubility-product constant.

4. The solubility product of $CaCO_3$ is 0.87×10^{-5} at 25°C. Calculate the molarity of the solution and the solubility of $CaCO_3$.

5. If we have 100 ml. of an $0.001M$ solution of $AgNO_3$ and if 100 ml. of $0.001M$ HCl is added, compute the concentration of the Ag^+ that remains unprecipitated. If 0.1 ml. of the HCl is used in excess, what would be the concentration of Ag^+, which remains unprecipitated?

6. What concentration of HCl is necessary to prevent the precipitation of CdS by $S^{=}$?

7. What is the hydronium ion concentration of 1 l. of an $0.05M$ solution of acetic acid to which has been added 100 ml. of $0.1M$ solution of sodium acetate? Calculate the pH.

8. How many ml. of a $2M$ solution of sodium acetate must be added to a liter of an $0.02M$ solution of acetic acid in order to make the pH of the solution 7.0?

9. Using the data from Prob. 4, calculate the concentration of Ca^{++} that must be added to a solution of CO_2 at 30°C. and 1 atm. pressure in order just to form a precipitate? (Solubility of CO_2 at 30°C., 0.1257 g./100 g. of water.)

CHAPTER IX

REACTIONS OF CHEMICAL COMPOUNDS

IV. OXIDATION-REDUCTION REACTIONS

To predict the outcome of reactions or even to predict the discovery of facts as yet unknown is more or less routine for the scientist; even a third-rate scientist must be fairly proficient in this art. We shall now consider some rarer achievements that demand either genius or considerable luck and sometimes both. When Louis Pasteur showed that the lowly yeast cells were responsible for the fermentation of grape juice, he not only explained the making of wine but, more significantly, correlated two sets of facts that had seemed until then to be unrelated. Such a correlation, taken from a different field, will provide the subject matter of this chapter. We propose to study this question: Are there any direct relationships among phenomena, such as the disappearance of the permanganate color upon the addition of ferrous ions and the electric current that flows through the wires in our streets and homes and that dispels the darkness and runs our vacuum cleaners?

The Experimental Basis.—In order to answer this question, we must first describe the peculiar type of chemical reaction that we wish to study. All students of qualitative analysis have at one time or another performed the test for the stannous ion with mercuric chloride solution. The presence of the stannous ion is indicated by the formation of a white precipitate that slowly turns gray and then black. The reactions that occur can be represented by the following equations:

$$2Cl^- + 2Hg^{++} \rightarrow Hg_2Cl_2 \rightarrow 2Hg^0 + 2Cl^-$$

Essentially, the reactions amount to this: the stannous ion has gained positive charges, and the mercuric ion has lost positive charges. We are accustomed to calling the gain of positive charges (or increase in the valence number) oxidation[1] and the loss of positive charges (or decrease

[1] The term oxidation, with its suggestion of oxygen, has been retained out of respect for the pioneering work of Lavoisier, who thought that oxidation invariably involves union with oxygen. At present, we use the term oxidation to characterize a much wider range of phenomena.

in valence number) reduction. Thus far, we have only a definition, no attempt having been made to determine how this change in the positive charge has been brought about. Let us remember, however, that *no oxidation is possible if a reduction does not occur simultaneously.* It is very much like a transaction on the Stock Exchange; the gain of Mr. *X* must be accompanied by a loss on the part of Mr. *Y*.

Let us illustrate this point with another example. When gaseous chlorine is passed into a solution containing ferrous ions, we find that the following changes take place:

$$Cl_2 \rightarrow 2Cl^-$$

Again, the oxidation of the ferrous ion has proceeded simultaneously with the reduction of the chlorine. Note that the substance that is being reduced, the chlorine, can be called an oxidizing agent, since it is the means by which ferrous ion is being oxidized, and similarly, the ferrous ion that is being oxidized can be called a reducing agent.

The Electronic Explanation.—The next question to be answered is, what happens structurally to an atom when it gains an additional positive charge? We already know the answer to this question from a previous discussion. Let us recall the transformation of the sodium atom into the sodium ion. The electrically neutral sodium atom, having 11 positive charges on the nucleus neutralized by 11 electrons in its electronic orbits, *lost* 1 electron, thus leaving 11 positive charges and 10 electrons. The net effect was that the sodium ion, thus produced, had a charge of +1.

$$Na^0 - \qquad Na^+$$

Using the same kind of electronic bookkeeping for Fe^{++}, we should say that the loss of one electron leads to Fe^+

$$Fe^{++} - 1\epsilon \rightarrow Fe$$

We can now define oxidation as the loss of electrons and reduction as the gain of electrons. In oxidation-reductions systems, some ions or atoms gain electrons, which are, in turn, lost by other ions or atoms; however, the whole system remains electrically neutral, as it was from the start.

THE CORRELATION

Now an interesting point arises; oxidation and reduction seem to involve the transfer of electrons from one substance to another. We know of another case wherein the transfer of electrons occurs, namely, in the passage of the electric current through a wire. Now, then, is

there any correlation between these two phenomena? Is it necessary that the electrons be furnished by another substance in contact with it, or can we use an electric current to supply the electrons?

The Experimental Evidence.—The easiest way and the scientific way to find out is to make an experiment. Into each of two beakers *A* and *B*, *A* containing a solution of ferrous chloride and *B* containing a solution of ferric chloride, let us immerse a wire. Next, we shall connect the wire from beaker *B* to the negative pole of a battery and that

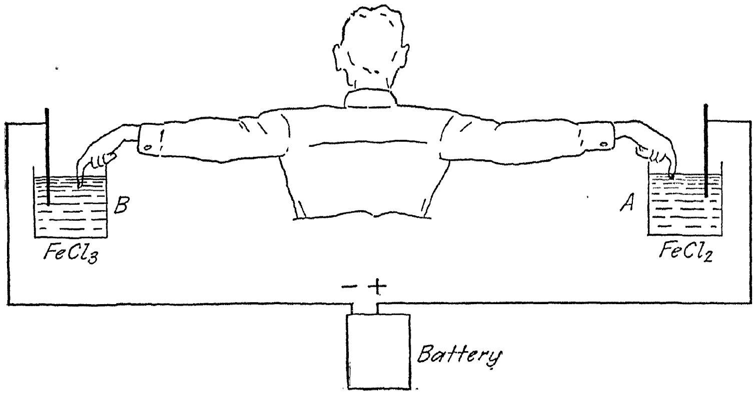


FIG. 38.—Oxidation and reduction by an electric current.

from beaker *A* to the positive pole of the battery. To complete the circuit, let us now dip a finger from one hand into the solution in beaker *A* and a finger from the other hand into the solution in beaker *B*. After a little while, if we test for the presence of ferric ion in beaker *A*, we shall find it present, and similarly, we shall find ferrous ion in beaker *B*. Here, indeed, we have proved that ferrous ion can be converted to ferric ion by the removal of electrons and vice versa. Evidently, then, oxidation-reduction is an electrical phenomenon and can be brought about by an electric current through the transfer of electrons.

However, we know that if we put ferrous and ferric ions together in one beaker, nothing will apparently happen. However, if we mix other substances, such as stannous chloride and mercuric chloride, there will be spontaneous oxidation and reduction. The question then presents itself, does the stannous chloride, of necessity, have to be in contact with the mercuric chloride, *i.e.*, be in the same beaker? To answer this question, let us again perform an experiment. Let us take two beakers, fill one with stannous chloride solution and the other with

mercuric chloride solution, dip a wire into each, connect the wires to a galvanometer, and dip a finger into each beaker to complete the circuit. The galvanometer needle will be deflected, showing the passage of current, and mercury and mercurous chloride will be in one of the beakers, showing that the oxidation and reduction are proceeding. Now we have proved the point that we wished to prove, namely, that a spontaneous oxidation-reduction actually means that electrons are being transferred and that the transfer can be from ion to ion or through an intervening external circuit.

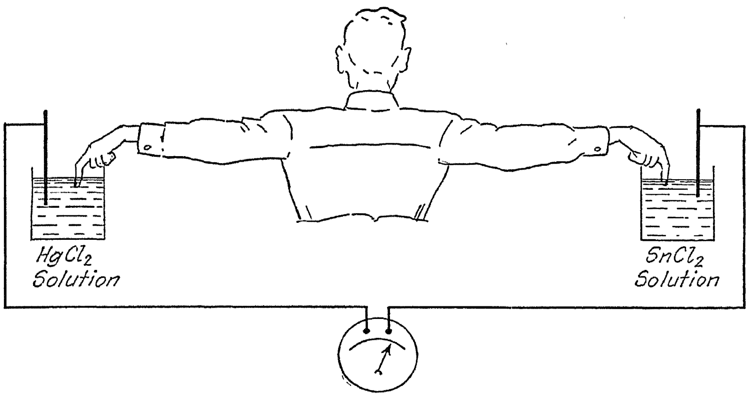


FIG. 39.—Production of a flow of electrons by a spontaneous oxidation-reduction.

The Salt Bridge.—One question still remains obscure. The inquiring student may ask, if the oxidation-reduction proceeds through the transfer of electrons, why do we need to complete the circuit by inserting a finger into each beaker? The answer is not too difficult to find. In the first experiment, in the beaker containing the ferric chloride, we had three chloride ions for every ferric ion, and hence the solution was electrically neutral. If we reduced some of the ferric ion to ferrous ion, there would have been an excess of chloride ion, since we need but two chloride ions for every ferrous ion; hence the solution would have been negatively charged. This charge would have opposed the further flow of electrons into the solution; hence we provided an exit for the excess chloride ions through our body. Similarly, the other beaker would have been lacking in chloride ion, and we therefore supplied them through our body.

A better practice than using the human body as a return circuit would have been to connect each beaker to a reservoir containing a large number of ions. For instance, we could have connected each

beaker to the ocean by means of a wet rag containing an electrolyte. In this case, the beakers could have been separated by miles of distance, with only a wire connecting them.

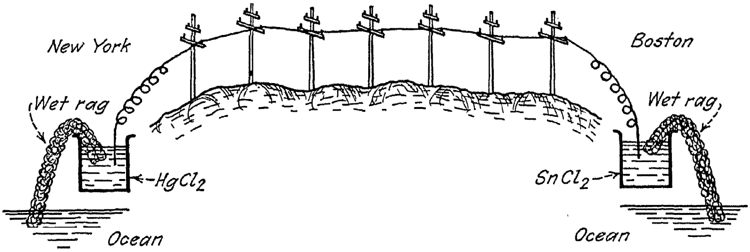


FIG. 40.—Oxidation and reduction using the ocean as a reservoir for ions.

A still better method, which is generally used in laboratories, is to connect the two solutions by a salt bridge. A salt bridge is merely a glass tube, filled with a saturated solution of an electrolyte (usually KCl), which is closed by a glass stopcock, or a glass plug. This obstruction prevents gross diffusion of the solution but does not prevent the migration of the excess ions.

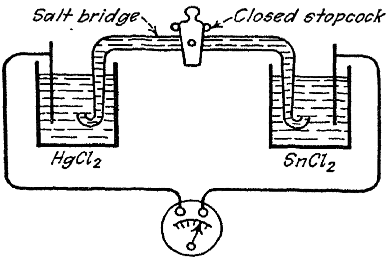


FIG. 41.—Oxidation and reduction using a salt bridge.

Formal Definitions.—As a conclusion, we should again state formally the definitions of oxidation and reduction. **Oxidation** is the loss of electrons by an atom or ion, or the algebraic increase in the valence number of the element. **Reduction** is the gain of electrons by an atom or ion, or the algebraic decrease in the valence number of the element.

BALANCING OXIDATION-REDUCTION EQUATIONS

The simple oxidation-reduction equations can usually be balanced by trial. However, when more complicated equations are encountered, the simpler methods are extremely tedious and uncertain and, indeed, often give us equations that, although they are balanced in the sense that the same number of atoms of each element appear on each side of the equation are, nevertheless, incorrectly balanced, since they do not represent what actually happens. However, by using the method described in the following pages, one can balance all oxidation-

reduction reactions with dispatch and with the certainty that they will be correct stoichiometrically.

Example 1.—Let us first take a very simple case that can be rapidly balanced by inspection and see how the method works.

Skeleton equation:

$$SnCl_2 + HgCl_2 \rightarrow Hg_2Cl_2 + SnCl_4 \qquad (1)$$

Let us first write this ionically:

Skeleton equation:

$$Sn^{++} + 2Cl^- + Hg^{++} + 2Cl^- \rightarrow Hg_2Cl_2 + Sn^{++++} + 4Cl^- \qquad (2)$$

Next let us determine which ions have been reduced and which ones oxidized. This can often be done by inspection or, in more complicated cases, by calculating the valence numbers of each element and then finding by inspection which valence numbers have increased and which ones have decreased. In this case, tin has gone from a valence number of +2 in Sn^{++} to +4 in Sn^{++++}; hence it has been oxidized. Writing the equation for this partial or half reaction, we get

$$Sn^{++} - 2\epsilon \rightarrow Sn^{++++} \qquad (3)$$

We must subtract two electrons from the left-hand side of the equation in order to make both sides equal in electrical charge. The mercuric ion has been reduced, going from +2 in Hg^{++} to +1 in Hg_2Cl_2. Again writing the half equation, we get

$$2Cl^- + 2Hg^{++} + 2\epsilon \rightarrow Hg_2Cl_2 \qquad (4)$$

Adding equations (3) and (4), we get

$$2Cl^- + 2Hg^{++} + Sn^{++} + 2\epsilon - 2\epsilon \rightarrow Hg_2Cl_2 + Sn^{++++} \qquad (5)$$

The electrons that we have added and subtracted cancel, and we get

$$2Cl^- + 2Hg^{++} + Sn^{++} \rightarrow Hg_2Cl_2 + Sn^{++++} \qquad (6)$$

Equation (6) tells us that every stannous ion reduces two mercuric ions to one mercurous chloride molecule. This equation (6), as written, has, however, a +4 charge on each side of the equation. To write a reaction between neutral salts, we must add four chloride ions to each side and so render each side neutral, as

$$6Cl^- + 2Hg^{++} + Sn^{++} \rightarrow Hg_2Cl_2 + Sn^{++++} + 4Cl^- \qquad (7)$$

Example 2.—Let us now take a more complicated case and go through the same steps.

Skeleton equation:

$$KMnO_4 + FeSO_4 + H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O \quad (8)$$

Written ionically

Skeleton equation:

$$K^+ + MnO_4^- + Fe^{++} + SO_4^{=} + H_3O^+ \rightarrow Mn^{++} + SO_4^{=} + Fe^{+++} + K^+ + H_2O \quad (9)$$

$$\text{Valence number of manganese in } MnO_4^- = +7$$
$$\text{in } Mn^{++} = +2$$

The permanganate ion has been reduced.

$$\text{Valence number of iron in } Fe^{++} = +2$$
$$\text{in } Fe^{+++} = +3$$

The ferric ion has been oxidized.
The half equations are

$$8H_3O^+ + MnO_4^- + 5\epsilon \rightarrow Mn^{++} + 12H_2O \quad (10)$$
$$Fe^{++} - 1\epsilon \rightarrow Fe^{+++} \quad (11)$$

NOTE: To balance equation (10), we added hydronium ion, which we combined with the oxygen of the permanganate ion to form water. This may not be the true mechanism, but it is conventionally agreed that we shall do this except where the equation indicates that it is impossible.

Equations (10) and (11) are not, however, electrically equal, and if we added them as such, the electrons that we have added and subtracted would not cancel; hence we multiply equation (11) by 5 and then add the two equations.

$$8H_3O^+ + MnO_4^- + 5\epsilon \rightarrow Mn^{++} + 12H_2O$$
$$5Fe^{++} - 5\epsilon -$$
$$8H_3O^+ + MnO_4^- + 5Fe^{++} \rightarrow Mn^{++} + 12H_2O + 5Fe^{+++} \quad (12)$$

This is the equation for the oxidation-reduction. The complete equation may now be written by inspection.

$$K^+ + MnO_4^- + 5Fe^{++} + 8H_3O^+ + 9SO_4^{=} \rightarrow Mn^{++} + 9SO_4^{=} + 5Fe^{+++} + 12H_2O + K^+ \quad (13)$$

Example 3.

Skeleton equations:

$$CrCl_3 + MnO_2 + H_2O \rightarrow MnCl_2 + H_2CrO_4 \quad (14)$$
$$Cr^{+++} + Cl^- + MnO_2 + H_2O \rightarrow Mn^{++} + Cl^- + H_3O^+ + CrO_4^{=} \quad (15)$$

Half equations:

$$12H_2O + Cr^{+++} - 3\epsilon \rightarrow CrO_4^{=} + 8H_3O^+ \quad | \; 2 \; | \qquad (16)$$
$$4H_3O^+ + MnO_2 + 2\epsilon \rightarrow Mn^{++} + 6H_2O \quad | \; 3 \; | \qquad (17)$$

. . . .

$$24H_2O + 2Cr^{+++} - 6\epsilon \rightarrow 2CrO_4^{=} + 16H_3O^+ \qquad (18)$$
$$12H_3O^+ + 3MnO_2 + 6\epsilon \rightarrow 3Mn^{++} + 18H_2O \qquad (19)$$
$$6H_2O + 2Cr^{+++} + 3MnO_2 \rightarrow 2CrO_4^{=} + 4H_3O^+ + 3Mn^{++} \qquad (20)$$
$$6H_2O + 2Cr^{+++} + 6Cl^- + 3MnO_2 \rightarrow 4H_3O^+ + 2CrO_4^{=} + 3Mn^{++} + 6Cl^- \qquad (21)$$

Example 4.

Skeleton equations:

$$KMnO_4 + MnSO_4 + H_2O \rightarrow K_2SO_4 + MnO_2 + H_2SO_4 \qquad (22)$$
$$K^+ + MnO_4^- + Mn^{++} + SO_4^{=} + H_2O \rightarrow K^+ + SO_4^{=} + MnO_2 + H_3O^+ \qquad (23)$$

It is evident here that the permanganate ion is being reduced to MnO_2 and that the manganous ion is being oxidized to MnO_2.

Half equations:

$$MnO_4^- + 4H_3O^+ + 3\epsilon \rightarrow MnO_2 + 6H_2O \quad | \; 2 \; | \qquad (24)$$
$$Mn^{++} + 6H_2O - 2\epsilon \rightarrow MnO_2 + 4H_3O^+ \quad | \; 3 \; | \qquad (25)$$
$$2MnO_4^- + 3Mn^{++} + 6H_2O \rightarrow 4H_3O^+ + 5MnO_2 \qquad (26)$$
$$2K^+ + 2MnO_4^- + 3Mn^{++} + 6H_2O + 3SO_4^{=} \rightarrow 4H_3O^+ + 3SO_4^{=} + 2K^+ + 5MnO_2 \qquad (27)$$

Example 5.

Skeleton equations:

$$Hg + HNO_3 \rightarrow Hg(NO_3)_2 + H_2O + NO \qquad (28)$$
$$Hg^0 + H_3O^+ + NO_3^- \rightarrow Hg^{++} + NO_3^- + H_2O + NO \qquad (29)$$

Half equations:

$$Hg^0 - 2\epsilon \rightarrow Hg^{++} \quad | \; 3 \; | \qquad (30)$$
$$4H_3O^+ + NO_3^- + 3\epsilon \rightarrow NO + 6H_2O \quad | \; 2 \; | \qquad (31)$$
$$3Hg^0 + 8H_3O^+ + 2NO_3^- \rightarrow 3Hg^{++} + 2NO + 12H_2O \qquad (32)$$
$$3Hg^0 + 8H_3O^+ + 8NO_3^- \rightarrow 3Hg^{++} + 6NO_3^- + 2NO + 12H_2O \qquad (33)$$

Example 6.

Skeleton equations:

$$AuCl_3 + H_2O_2 + NaOH \rightarrow NaCl + H_2O + O_2 + Au \qquad (34)$$
$$Au^{+++} + Cl^- + H_3O^+ + O_2^{=} + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O + O_2 + Au^0 \qquad (35)$$

Half equations:

$$- 3\epsilon \rightarrow Au^0 \quad (36)$$
$$- 2\epsilon \rightarrow O_2 \quad (37)$$
$$\overline{3O_2^{=} \rightarrow 2Au^0 + 3O_2} \quad (38)$$
$$6Cl^- + 6Na^+ + 6H_3O^+ + 6OH^- + 3O_2^{=} \rightarrow$$
$$2Au^0 + 3O_2 + 12H_2O + 6Na^+ + 6Cl^- \quad (39)$$

Example 7.

Skeleton equations:

$$CoCl_2 + KOH + H_2O_2 \rightarrow KCl + Co(OH)_3 \quad (40)$$
$$Co^{++} + Cl^- + K^+ + OH^- + H_3O^+ + O_2^{=} \rightarrow$$
$$K^+ + Cl^- + Co(OH)_3 + H_2O \quad (41)$$

Half equations:

$$3OH^- + Co^{++} - \epsilon \rightarrow Co(OH)_3 \quad 2 \quad (42)$$
$$O_2^{=} + 2H_2O + 2\epsilon \rightarrow 4OH^- \quad 1 \quad (43)$$
$$\overline{2OH^- + 2Co^{++} + O_2^{=} + 2H_2O \rightarrow 2Co(OH)_3} \quad (44)$$
$$4Cl^- + 4K^+ + 4OH^- + 2H_3O^+ + O_2^{=} + 2H_2O \rightarrow$$
$$2Co(OH)_3 + 4K^+ + 4Cl^- + 4H_2O \quad (45)$$

THE MEASUREMENT OF THE OXIDIZING POWER

One other problem is yet to be considered, namely, if we wish to oxidize a substance in the laboratory, can we choose any known oxidizing agent? Upon consideration, the answer will be, no, we cannot choose any oxidizing agent. For although it is true that the primary purpose of an oxidizing agent is to gain electrons and so be reduced, we must remember that we are dealing here, as always, with opposing tendencies—the tendency of an ion to gain electrons or to lose them. If we mix two substances that can either gain or lose electrons, the one that has the greater attraction for electrons will gain them at the expense of the other. If now we take the substance that in this first reaction has been shown to be able to lose electrons and put it in the presence of a substance that loses electrons still more readily, it will gain them. A good example of an ion that does this readily is the nitrite ion. In the presence of the iodide ion, the nitrite ion acts as an oxidizing agent.

$$2I^- - 2\epsilon \rightarrow I_2$$
$$2H_3O^+ + NO_2^- + \epsilon \rightarrow NO + 3H_2O$$

But in the presence of the permanganate ion, which is a stronger oxidizing agent, the nitrite ion acts as a reducing agent.

$$8H_3O^+ + MnO_4^- + 5\epsilon \rightarrow Mn^{++} + 12H_2O$$
$$3H_2O + NO_2^- - 2\epsilon \rightarrow NO_3^- + 2H_3O^+$$

Accordingly, we are interested in the question, how strong is an oxidizing agent, or how great an affinity does it have for electrons? In order to answer this question adequately, we must investigate the devices that permit the measurement of the oxidizing power of a substance.

Since the oxidizing power is concerned with the intensity of the desire of the ions to gain electrons and since an electron flow is an electric current, measuring the intensity of the electric current, *i.e.*, its potential, will provide us with an answer. Suppose that we have in a beaker a solution of a strong oxidizing substance, such as ceric sulfate. Ceric ions, Ce^{++++}, tend to acquire electrons giving cerous ions, as

$$Ce^{++++} + \epsilon -$$

When we begin our experiment, the oxidized form Ce^{++++} is overwhelmingly preponderant, and the concentration of the reduced form Ce^{+++} is practically negligible. On introducing a platinum electrode into this solution, what will happen? Ceric ions will remove some electrons from the platinum electrode, and the electrode will acquire a positive charge. Now we wish to measure the magnitude of this charge. We must remember, however, that this electrical potential, the intensity factor of electrical energy, can be measured only if it is compared with another known potential. We therefore connect the ceric half cell with another beaker containing a reference electrode, *i.e.*, an electrode that maintains a constant charge. Suppose we now find that the difference between the potentials of the platinum electrode in the ceric solution and the reference electrode is +1.70 volts. We can now say, let us take the potential of the reference electrode to be zero; hence the potential of this ceric solution is +1.70 volts.

This assumption is a defensible one. The same assumption is made in measuring the intensity factor of heat energy, the temperature, where the melting point of ice is taken to be zero and all other temperatures are measured relative to it.

Reference Electrodes.—In our experiment, we used an electrode that would maintain an unvarying potential. The electrode that has been chosen as the reference electrode and hence has been assigned a potential of zero is the hydrogen electrode. It consists of a platinum electrode, over which flows gaseous hydrogen at 1 atm. pressure. The platinum is coated with platinum black, which is finely divided platinum metal. This platinum black serves as a catalyst, accelerating the attainment of equilibrium. The electrode is in contact with an acidic

solution having a hydronium ion activity of 1 (*i.e.*, $[H_3O^+]$ of 1 approximately). Let us now see why a constant potential is maintained under these conditions by this half cell. The hydrogen molecules absorbed on the electrode lose electrons giving hydronium ions to the solution thus:

$$2H_2O + H_2 - 2\epsilon \rightarrow 2H_3O^+$$

The electrode thus acquires a negative charge, but the reverse reaction also occurs, namely, hydronium ions gain electrons from the electrode and form hydrogen, as

$$2H_3O^+ + 2\epsilon \rightarrow H_2 + 2H_2O$$

This tends to impart a positive charge to the electrode. After equilibrium has been attained, the two reactions will impart to the electrode a definite potential, which will remain constant as long as the concentrations of the H_2 and the H_3O^+ remain unchanged.

If need be, we can, by the use of such a reference electrode, calibrate other reference electrodes, whose potential we shall then know. One of the most common auxiliary reference electrodes used is the calomel electrode. It consists of mercury covered by a paste of mercurous chloride, potassium chloride, and mercury in contact with a solution saturated with mercurous chloride and potassium chloride. Contact is made with the mercury by means of a platinum wire.

Molar Potentials.—Now let us return to our example, in which a solution containing cerous and ceric ions in contact with a platinum electrode is connected to our standard reference electrode. In our example, the ceric ions were preponderant, and the reduced form, the cerous ions, were almost absent. Let us now investigate this point. Would changes in the ratio $\frac{Ce^{++++}}{Ce^{+++}}$ affect the potential? If we made a large number of potential measurements, increasing in each experiment the concentration of the reduced form Ce^{+++} at the expense of the oxidized form Ce^{++++}, we would find experimentally that the potential would fall in direct proportion to the decrease in this ratio. Evidently, then, the value of this ratio has an effect on the value of the potential developed. If now we wish to compare the potential developed by different oxidizing agents, we must choose some ratio as a standard; otherwise the comparisons will be valueless. The simplest ratio, 1, has been chosen. In our case, when the concentration of the ceric ion is equal to the concentration of the cerous ion, their ratio equals one. The potential developed by this cell is called the molar potential and is usually indicated by E_0.

The outstanding usefulness of the molar potential can easily be shown. It enables us to catalogue all the oxidizing systems according to their oxidizing power. For instance, one can decide the following question: Which is the stronger oxidizing agent, ceric sulfate or potassium dichromate? We need merely look up their molar potentials in the appropriate tables. The value for $\frac{Ce^{++++}}{Ce^{+++}} = +1.45$; that for $\frac{Cr_2O_7^{=}}{Cr^{+++}} = +1.3$. This really means that under identical concentration conditions, the ability of the ceric ions to acquire electrons is greater than that of the dichromate ions, since its electrode becomes more positive. Hence the ceric ion is a stronger oxidizing agent.

TABLE XVIII.—MOLAR POTENTIALS FOR OXIDIZING AGENTS

Oxidized form	Reduced form	E_0	Oxidized form	Reduced form	E_0
MnO_4^-	Mn^{++}	+1.5	Cu^{++}	Cu^0	+0.34
Ce^{++++}	Ce^{+++}	+1.45	Sn^{++++}	Sn^{++}	+0.14
Cl_2	Cl^-	+1.36	H_3O^+	H_2	0.0
$Cr_2O_7^{=}$	Cr^{+++}	+1.3	Sn^{++}	Sn^0	−0.13
Fe^{+++}	Fe^{++}	+0.75	Fe^{++}	Fe^0	−0.44
I_2	I^-	+0.54	Zn^{++}	Zn^0	−0.76
Cu^{++}	Cu^+	+0.46			

READING REFERENCES

GLASSTONE, S.: "Electrochemistry of Solutions," pp. 328–359, D. Van Nostrand Company, Inc., New York, 1930.

HAMMETT, L. P.: "Solutions of Electrolytes," 2d ed., Chaps. VI and VII, McGraw-Hill Book Company, Inc., New York, 1936.

LATIMER, W. M.: "Oxidation Potentials," Prentice-Hall, Inc., New York, 1938.

JETTE, E.: "Oxidation-Reduction Reactions," The Macmillan Company, New York, 1927.

LATIMER, W. M., and J. H. HILDEBRAND: "Reference Book of Inorganic Chemistry," rev. ed., pp. 471–481, The Macmillan Company, New York, 1940.

QUESTIONS

1. Balance the following equations by the ion-electron method:

a. Hg_2Cl_2 + aqua regia $\rightarrow$

b. $Mn^{++} + HNO_3 + NaBiO_3 \rightarrow$

c. $MnO_4^- + H_2O_2 \rightarrow Mn^{++} + O_2$
d. $SnS_3^= + Mg + H_3O^+ \rightarrow$
e. $Cr_2O_7^= + H_2S + H_3O^+ \rightarrow$
f. $VO^{++} + MnO_4^- \rightarrow VO_4^= + Mn^{++}$
g. $S_2O_3^= + C_2O_4^= \rightarrow SO_4^= + CO_2$
h. $IO_3^- + I^- + H_3O^+ \rightarrow I_2 + H_2O$
i. $SO_4^= + H_3O^+ + Cu \rightarrow$
j. $SO_4^= + H_3O^+ + I^- \rightarrow H_2S + I_2 + H_2O$
k. $P + OH^- \rightarrow H_2PO_2^- + PH_3$
l. $Fe(CN)_6^{\equiv} + H_2O_2 \rightarrow Fe(CN)_6^= + H_2O$
m. $Mn^{++} + Na_2O_2 \rightarrow MnO_2 + Na^+ + OH^-$

2. If you added Zn metal to a solution of Fe^{++}, would oxidation-reduction take place? Write the equation. If metallic Fe were added to Zn^{++} solution, what reaction would take place?

3. Arrange the following in order of their oxidizing power: Ce^{+++}, Sn^{++}, and n -

4. Arrange the following in descending order of oxidizing power: Fe^{+++}, Cu^{++}, Sn^{++}, and MnO_4^-.

5. How many grams of aluminum powder are needed to reduce 2 g. of $KClO_3$ to KCl?

6. Write equations showing what would happen if H_2S were passed into concentrated HNO_3; if it were passed in a solution of $K_2Cr_2O_7$.

PART II

EXPERIMENTAL

CHAPTER X

INTRODUCTION

One of the oldest branches of the science of chemistry is analysis. Its methods and techniques have been developed over a long period of time, from the crude furnaces and retorts of yesterday to the high-precision instruments of today. Because of the limitations of the original techniques, large quantities of material were required for analysis. With the improvement in methods, as time went on, the quantities were gradually decreased. Qualitative analysis followed this broad pattern and gradually became standardized so that it was customary to use from 15 to 25 ml. of solution for an analysis.

With the advent of modern biochemical research and toxicology, the necessity for developing a new technique for the manipulation and analysis of the minute amounts of potent substances isolated from natural sources became apparent. As a result, a microtechnique was evolved, wherein 1 to 5 drops of a liquid or 2 to 6 mg. of a solid, could be handled successfully. This method was later extended to all the fields of chemistry. This technique is rather complex, however, both in the equipment and in the manipulative skill required of the analyst.

The complexity of the technique led to a search for one that would combine the accuracy and speed of the micro methods with the simplicity of the classical methods and that could be taught successfully to the average undergraduate student. The solution was found in the semimicro method. As used in qualitative analysis, the student uses from 1 to 5 ml. of solution for an analysis. At the beginning of the course, the volume of solution taken for analysis is close to the higher figure; later, as the student's skill increases, the volume should approach the lower figure. Of course, allowance must be made for the complexity of the unknown sample.

Semimicro qualitative analysis, as described in this book, uses the classical hydrogen sulfide scheme with some modifications. Some of the recently developed reactions using organic reagents are employed as confirmatory tests. This is not so radical an innovation as may appear, since organic reagents for nickel and cobalt have long been known and used. However, the indiscriminate use of organic reagents for most tests has been avoided, since experience has shown that many

of the inorganic tests are equally sensitive and are better adapted for teaching the principles of inorganic chemistry.

In keeping with the basic principles underlying semimicro analysis, the necessary apparatus has purposely been kept simple and the smaller sizes of standard equipment used as much as possible. The special items may now be purchased relatively inexpensively or may be constructed by the student in his spare time.

Although many varieties of apparatus found in the literature may be employed in semimicro qualitative analysis, the authors have found by experience that these generally exhibit no superiority to those described in the body of the book.

CHAPTER XI

MENTAL ATTITUDE

Not so long ago, qualitative analysis, together with quantitative analysis, was definitely a "bread-and-butter" course, by the use of which most chemists earned their livelihood. Nowadays, the control of technical operations has to a large extent veered from the long-drawn-out chemical procedures to the shorter physical methods, such as the spectrographic and polarographic techniques. Qualitative analysis, far from having lost its importance as a teaching tool, now has acquired additional aims. Qualitative analysis has as its objectives the following:

1. To furnish practical examples of the operations of the laws of chemistry.
2. To furnish a body of facts pertaining to inorganic chemistry.
3. To increase the manipulative skill of the student.
4. To develop the scientific attitude.
5. To serve as an introduction to the research ideology.

A number of theoretical ideas have been presented to the student regarding the fundamental laws and hypotheses of chemistry. The laboratory work in this text offers a practical demonstration of the application of many of these laws. In addition, the student has an opportunity to acquire a large number of facts concerning the chemistry of inorganic compounds. This entails the performance of a considerable number of experiments, in the course of which the student has ample opportunity to increase and improve his manipulative skill and technique.

The scientific attitude is based upon pertinent observations made in the course of experimental work, deductions drawn therefrom, and conclusions arrived at after coordination of all the evidence. Pertinent observations are those pertaining to the formation, form, and color of precipitates; the evolution, color, and odor of gases; and any other changes apparent in the material under consideration. The art of observation may be acquired by the student. To further this aim, the preliminary experiments contain only a few references to the expected results.

Yet, the mere gathering of observations is in itself but a beginning. The situation may be compared with that of a detective gathering

clues. Experimental observations (like clues) are of no value unless the proper deduction can be drawn from them. For example, an observation by the student that his unknown solution is colorless should immediately lead to the deduction that colored ions, such as cupric, nickel, and chromate, are probably absent. If the solution is neutral, salts of the weak acid-strong base type, and vice versa, are also probably not present.

The student should note carefully that the word probably is used. Any single piece of evidence is usually insufficient ground on which to base a conclusion. Let us refer once more to the example of the detective; if he walks into a room, sees a man lying on the floor and a gun on the table, he has two clues (observations) and may therefore conclude that the man has been shot. This deduction may or may not be valid, however, and cannot be accepted as a conclusion until supporting evidence is obtained. Similarly, before drawing a conclusion in chemical analysis, the student must have a mass of evidence that is predominantly in favor of the conclusion he draws. Some of the deductions may point directly to the conclusion; others may be diametrically opposed; but on the whole, the evidence should be cumulative in the right direction. The conclusion must be reached on the basis of the impartial weighing of facts. The scientific attitude demands this impartial weighing of facts without permitting the intrusion of preconceived notions and ideas.

If the student adopts this attitude in investigating a troublesome point in the analysis, *e.g.*, the unexpected appearance of a precipitate, he proceeds to make a series of experiments designed to disclose the nature of the precipitate. From the results obtained, the student may logically explain his difficulty. **The student is now doing research.** True, the point may be trivial and the facts well known, but from the student's point of view, it is research. Research, with a capital R, is merely the extension of this attitude and method to problems lying at and beyond the boundary of present-day scientific knowledge. This point cannot be overstressed. Research is not a course that can be completed in so many hours but is the result of an attitude acquired by the student in the course of his chemical work. The research ideology extended to more complex problems, involves first, a search of the chemical literature to ascertain what is known and what has been done on the subject; then a series of experiments based on this knowledge is made, and certain deductions are drawn. More experiments are then carried out to test the validity of these deductions. Finally, the evidence is weighed carefully and impartially and a conclusion drawn.

Similarly, the student doing his unknowns should consider his laboratory manual and other more comprehensive textbooks as the recorded chemical knowledge for his purpose. On this basis, experiments are performed on the unknown and deductions drawn therefrom; the deductions are tested by further experimentation, and finally, conclusions are made as to the presence of certain substances.

The authors have found that the analysis of solutions whose composition is known, as a preliminary to analysis of the unknown, is unsatisfactory. This is so since, generally, the student does not then regard the "known" unknown as a minor research problem but thinks of it rather as something to be done in cookbook fashion. This attitude is usually carried over to the analysis of the actual unknown. Also, in analyzing the known, the student may get a vague or indefinite test but does not check it, since he already knows whether the ion in question should be present. This may lead to an incorrect conclusion when the unknown is analyzed. In using the research idea, if the test is vague, the student will repeat the test, running simultaneously a control test and a blank.

A **control test** is one that is performed exactly as given in the analytical procedure, except that a sample of the ion in question is used instead of the unknown. A **blank test** is a repetition of the given test, using all the reagents but omitting both the unknown and known samples of the ion. These two tests, together with the actual test on the unknown, should be run simultaneously and compared whenever the result is doubtful.

The research ideology demands that the student be aware of the reason for each step in the analysis. Consequently, very detailed directions specifying exactly the amounts of this or that reagent or test solution are generally omitted. In many cases, however, the technique of the test involves the use of definite proportions of reactants, and in such cases detailed directions are, of course, given.

The Notebook.—One other fundamental principle of the research ideology has not yet been mentioned: the keeping of an accurate and complete written record of the experimental work. Results should be recorded immediately in ink in a *bound* notebook. The student should never trust his results to his memory or to slips of paper. The notebook page should be divided into three vertical columns. In the first column should be placed, as briefly as is consistent with clarity, what has been done. In the second column is recorded the observation of the chemical change. Finally, in the last column, there is recorded an explanation that may consist of an equation, the formula of the product, a deduction, or a conclusion. An equation should be written

eve It is not necessary for the student to notebook should be as brief as that it will be understood by a person and enable him to draw the same conclusions regarding an When an analysis has been com-

Test	Observation	Explanation
$Ag^+ + HCl$	white ppt:	$AgCl\downarrow$
$AgCl + NH_4OH$	soluble	$Ag(NH_3)_2^+ + Cl^-$
$Ag(NH_3)_2^+ + Cl^- + HNO_3$	white ppt.	$AgCl\downarrow$
		Ag present
Group II, III, IV, V neutralized	dark ppt:	basic salts and hydroxides
made up to 0.5 N with HCl	some ppt left	basic salts of group II
satd. with H_2S	black ppt then yellow	sulfides of group II
dilute to 0.3 N		
satd. with H_2S	yellow ppt	

FIG. 42.—Part of a notebook page.

pleted, a report should be submitted listing briefly the conclusions arrived at. Of course, this implies that the completed notebook is available for examination at the same time.

This chapter may be summarized with the statement that the crux of the course in qualitative analysis is the analysis of the unknown samples. These should be graduated in difficulty, and complexity and should serve as a test of the student's ability.

CHAPTER XII

APPARATUS AND TECHNIQUE

Most of the reactions of semimicro qualitative analysis are carried out in small Pyrex test tubes, followed by centrifugation and decantation of the supernatant liquid (filtration). Filtrates and solutions are evaporated in small porcelain crucibles. Confirmatory tests are performed on a spot plate, glass slide, or filter paper, depending upon the individual ion.

The authors have found experimentally in the laboratory that the most satisfactory method of generating hydrogen sulfide is by means of Aitch-Tu-Ess cartridges. This is far superior to the sulfide and acid method of generation in any of the various pieces of apparatus described in the literature and is also superior to bottled gas.

The various operations are described in detail in the following sections:

1. Reactions.—Reactions should be carried out, wherever possible, in vessels that will obviate the necessity of transferring the precipitate to another container for the next operation. When centrifugation and decantation, which will hereafter be called filtration, is the next step, the reaction should be carried out in Pyrex test tubes, either 10 by 75 mm. or 13 by 100 mm., depending upon the quantity of material used. When the reaction is to be used as a confirmatory test, it should be carried out (1) on a spot plate if the expected solution or precipitate is colored; (2) on a glass slide with a black background or in a black glazed crucible if the precipitate is white; and (3) on filter paper in special cases. If the filtrate from a particular reaction is to be evaporated, it should immediately be placed in a crucible. **Transfer of materials should be avoided wherever possible to eliminate losses.**

2. Precipitation.—The solution is placed in a test tube (unless subsequent operations indicate that some other vessel is more suitable) and the reagent added *dropwise* from a medicine dropper until no further apparent precipitation occurs. The test tube is then placed in the centrifuge and balanced (see the next paragraph) and centrifuged for about 15 seconds, or until the supernatant liquid is clear. Another drop of the reagent is then added. If no further precipitation occurs, the reaction is complete. Should more precipitate form, repeat the

foregoing procedure until no further reaction occurs. This important step is known as testing for *completeness of precipitation.*

3. Centrifuge.—The most desirable type of centrifuge for semimicro analysis is the constant-speed, angle-head electric centrifuge, holding two 10 by 75 mm. test tubes and two 13 by 100 mm. test tubes.

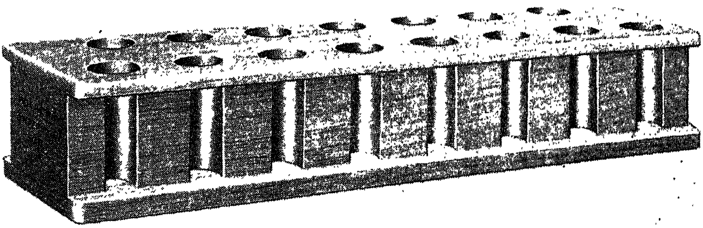


FIG. 43.—Test-tube rack. (*Courtesy of Wilkens Anderson Company.*)

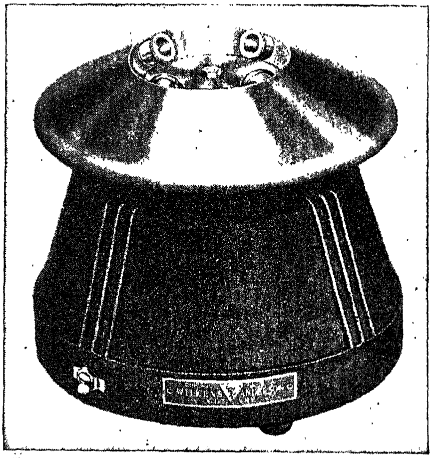


FIG. 44.—Centrifuge. (*Courtesy of Wilkens Anderson Company.*)

All centrifuges must be balanced when operating. When a tube is placed in the centrifuge, a second tube filled with an equal weight and volume of material should be placed in the exactly opposite aperture of the head. For the usual solutions, a tube filled with an equal volume of water is satisfactory. If this is not done, the centrifuge will vibrate excessively and this may lead to damage to the centrifuge and even to injury of other students because of the breaking of the tubes.

Hand centrifuges and electrical centrifuges having swinging tube holders may be used, although they are less desirable from the point of

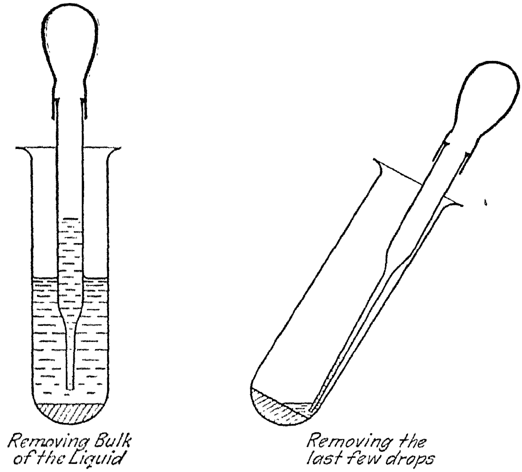


FIG. 45.—Filtration, usual method.

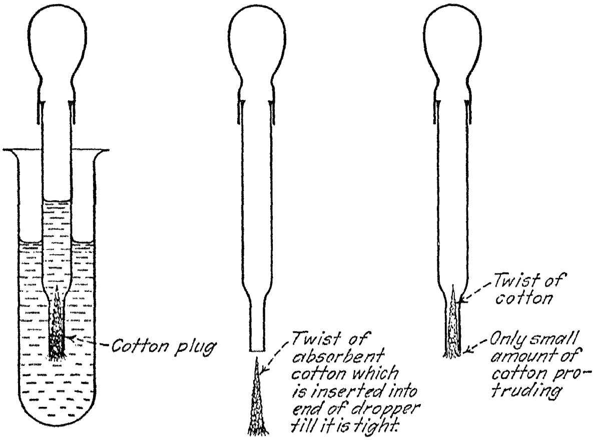


FIG. 46.—Filtration by the cotton-plug method. Used very occasionally when centrifugation is difficult.

view of speed of centrifugation and the requirement of additional safeguards.

4. Filtration.—After the solution and precipitate have been centrifuged, the precipitate is usually packed tightly in the bottom of the

tube. The bulk of the supernatant liquid is removed with a medicine dropper without disturbing the solid. The tube is tilted slightly and the remaining drop or two removed with a capillary dropper. If filtration is difficult with this method, recourse is often made to the cotton-plug method, which is illustrated in Fig. 46.

5. Washing of Precipitates.—Washing is usually performed to remove completely the last traces of the solution (filtrate). To the solid left in the tube after filtration, the wash liquor is added dropwise. The solution is stirred with a glass rod and centrifuged. The wash liquor is then removed as in filtration. The wash liquor is generally water but may be the reagent or some other appropriate liquid.

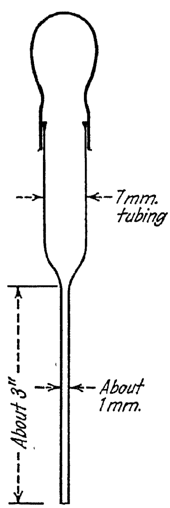


FIG. 47.—Micro dropper.

It is often necessary to test for completeness of removal of soluble ions. In such cases, the wash liquor is added in small portions, and after filtration, each successive portion is tested for the ion whose removal is desired. The washing is called "complete" when the last portion shows no appreciable quantity of the ion to be present. The washings are usually combined with the original filtrate. The volume of wash liquor used should be kept as small as possible. A large number of washings with small portions of wash liquor is more effective then a few washings with larger volumes, even though the total volume used is the same in both cases.

6. Droppers.—Medicine droppers and capillary droppers are used for the transfer of reagents from one vessel to another. The most desirable form of medicine dropper should have a straight glass tube 4 to 4½ in. long, tapered at the lower end. Droppers generally deliver from 15 to 30 drops per ml. Several droppers, delivering approximately 20 drops per ml., should be selected and roughly calibrated by the student, in half milliliters, against a graduated cylinder. A file scratch should be made at the appropriate points.

A number of capillary droppers should be made by the student, either by drawing out the ends of medicine droppers or from 7-mm. glass tubing by the method described under Reagent Bottles. The dropper should contain about 1 ml. of solution, and the tip should be approximately 1 mm. in diameter and 75 mm. (3 in.) in length. These droppers are used for removing the last drops of filtrate and for adding very small drops of solution.

All clean droppers, when not in use, should be kept in a beaker of clean distilled water. After use, they should be placed aside in another beaker for cleaning at an appropriate time. If the droppers are soiled with substances which cannot be removed by water and a brush, they should be washed in cleaning solution.

7. Transfer of Precipitates.—It is generally inadvisable to transfer precipitates from one vessel to another, since this leads to a loss of material. Although microspatulas, either of glass or metal, may be used, this method is not feasible, especially when small amounts of precipitate are to be transferred. A better method is to shake up the mixture of solid and liquid to obtain a uniform suspension and to transfer the suspension with a dropper to several test tubes. These may then be filtered in the usual manner. If a portion of the precipitate is to be placed on a spot plate or glass slide, a drop of the suspension is placed in the depression, the precipitate allowed to settle, and the solution removed with a capillary dropper. The clear liquid may also be removed by touching a piece of absorbent filter paper to the edge of the drop.

8. Extraction.—Extraction is a process very similar to washing. The difference is that in washing, the removal of a contaminant is desired, whereas in extraction, the separation of a particular substance is sought. The extracting liquid (usually not cold water) is added to the precipitate in small portions, the mixture stirred, warmed if necessary, and filtered. The process is repeated until no more material is extracted. This is determined by testing the last extract for the desired substance. In carrying out extractions, it is well to remember that no totally insoluble substance exists. Substances differ only in their degree of solubility. Therefore, it is necessary to exercise common sense in extracting a particular substance. Enough extracting liquid should be used so that only a negligible amount of the desired substance is left unextracted and only a small amount of the undesired substances are dissolved. The exact point at which an extraction may be considered complete must be determined empirically on the basis of experience.

9. Heating of Solutions.—There are several methods of heating solutions. If direct heat is necessary, a microburner is used. The test tube to be heated, which may be conveniently held in a wooden spring clothespin, is placed in the flame at an angle, the mouth of the tube being pointed away from the analyst and his fellow workers. The tube must be kept in continual motion to prevent superheating.

Test tubes are usually heated on the water bath. The most convenient type of water bath is about 4 in. in height and 3 in. in diameter.

The top has three holes, each approximately 1 in. in diameter. In these holes, corks are fitted, through which holes have been bored of such size as to accommodate test tubes. Several suitable types of water baths for semimicro analysis are available from laboratory supply houses. If it is desired to heat the solution to a particular temperature, a thermometer is placed in the water. If crucibles are to be heated on the water bath, the cork is removed and the crucible placed directly into the opening.

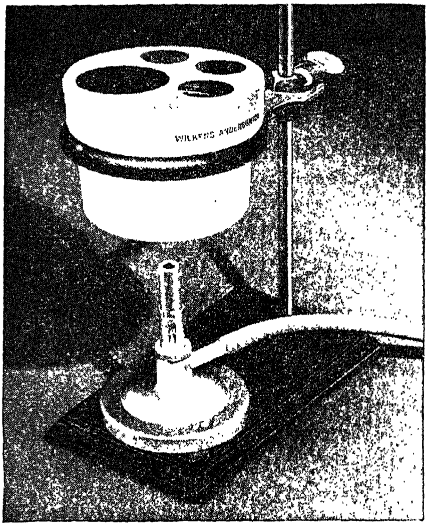


FIG. 48.—Water bath. *(Courtesy of Wilkens Anderson Company.)*

If evaporations are to be carried out at temperatures higher than that of boiling water, a porcelain or iron dish is filled with sand and the vessel to be heated (usually a crucible) is placed in the sand. Most evaporations are carried out in high-form crucibles, of a capacity of either 5 or 15 ml. Crucibles are used in preference to other vessels, since they are less subject to breakage and also provide a greater surface from which evaporation may take place.

When a solution is to be evaporated to dryness, it should be heated just to the point at which the residue is dry and should not be baked, since this may lead to undesirable chemical changes. Care should be taken in handling crucibles with tongs so that no iron or rust is introduced into the sample as contamination.

10. Generation of H_2S.—Hydrogen sulfide is best generated by the use of Aitch-Tu-Ess cartridges. The cartridge, which contains 5 g.

of material (equivalent to 1.25 l. of H_2S) is placed in a Pyrex test tube (20 by 150 mm.). The mouth of the tube contains a rubber stopper and delivery tube which leads to the bottom of a small side-arm test tube filled with absorbent cotton. This aids in the removal of any free sulfur that may be carried over with the gas. A thin rubber hose attached to the side arm holds the delivery tips, which are made in the same manner as capillary droppers. The delivery tips must be kept clean and should be used for only one precipitation. A number of these tips should be kept on hand.

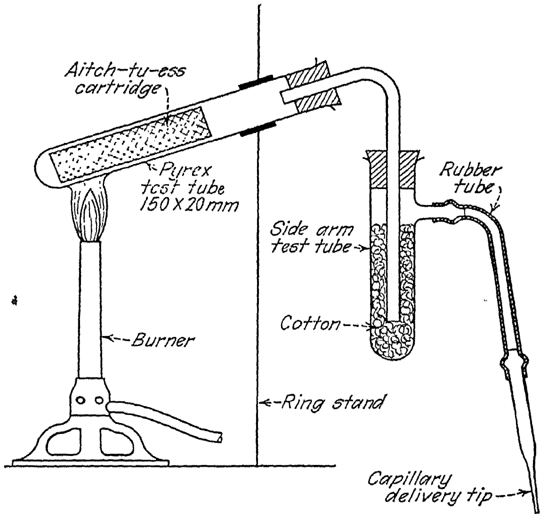


FIG. 49.—Individual H_2S generator using Aitch-Tu-Ess cartridges.

To generate H_2S, the Pyrex test tube is gently heated with a burner. When the heating is stopped, the flow of gas ceases almost immediately. Completeness of precipitation with H_2S is tested for in the usual manner. The amount of heat should be so adjusted that approximately 2 bubbles per second of H_2S are evolved. Heating too strongly leads to the sublimation of sulfur, which is undesirable. The student should remember that the apparatus is filled with air and that the first few milliliters of gas are not H_2S. **Hydrogen sulfide is quite toxic and should be handled with discretion.**

11. Reagent Bottles.—In this laboratory, for classes of from 20 to 30 students, a complete set of reagents (with certain exceptions) is kept on the side shelf. The solids are kept in 8-oz. widemouthed glass-

stoppered bottles. The liquids are kept in 32-oz. narrow-mouthed bottles, equipped with rubber stoppers and long dropping pipettes with rubber nipples (except for certain cases in which corks are used). These droppers, as well as capillary droppers and delivery tips, are made from 7-mm. soft-glass tubing constricted at one end by heating, with the top flattened by pressing the heated end on a piece of soapstone or on an asbestos board. The droppers should extend to the bottom of the reagent bottle. The rubber nipples may be purchased from any supply house. Concentrated acids are kept in 32-oz. glass-stoppered bottles at the end of each row of desks. Certain very expensive reagents, of which only very small quantities are used, are dispensed from the storeroom.

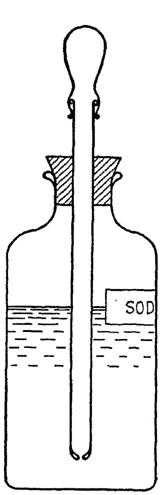


FIG. 50.—Reagent bottle.

Each student is provided with a kit of bottles consisting of four 2-oz. narrow-mouthed glass-stoppered bottles, which contain concentrated hydrochloric, sulfuric, and concentrated and dilute nitric acids, six 2-oz. bottles with medicine droppers, which contain dilute hydrochloric and sulfuric acids, concentrated and dilute ammonium hydroxide and concentrated and dilute acetic acid. (All dilute acids and alkalis are $6N$ and should be prepared by the student.) The student also receives four 1-oz. bottles and twelve ¼-oz. bottles, both types equipped with medicine droppers. These are used for the more common reagents and are filled by the student from the reagents on the side shelf.

Experience has shown that it is unnecessary to furnish the student more bottles than those listed above. The bottles are issued in cardboard boxes, which serve as containers for them during the course and which may then be discarded.

12. Spot Tests.—Spot tests are made on filter paper, because (1) very small volumes of solutions may be used and (2) the sensitivity of the test is generally increased.

When a drop of a solution is placed on filter paper, the liquid is absorbed by the paper, and the drop spreads. If another drop of a second liquid, which will react with the first to form a colored precipitate, is placed on the filter paper, it, too, will be absorbed and will spread. At the interface where the two drops meet, precipitation occurs, and as more liquid diffuses through the interface, the precipitate accumulates at this point, giving a greater intensity of color than would be obtained if the two drops were mixed on a spot plate. Furthermore,

the fact that many precipitates are adsorbed on the surface of the filter paper fibers often increases the intensity of the color.

Another technique is frequently employed in making spot tests. A drop of liquid is placed on filter paper and allowed to absorb completely. A second drop of liquid, which will produce a precipitate, is placed in the center of the first drop. At the circular interface, a ring of precipitate forms. If a drop of water is now added to the center of the wet spot, it is absorbed and forces the unreacted constituents of the first drop away from the precipitate. Another precipitant may now be added, and a ring of a different color will be formed outside the first one. In this manner, one drop of solution may be tested for several constituents successively. It is important, however, that every drop of liquid added to a spot on filter paper should be allowed to absorb completely before the next drop is added. The succeeding drops should usually be added at the exact center and should cover as small an area as possible; *i.e.*, all the drops should theoretically start from a mathematical point and diffuse outward.

A good grade of filter paper should be used for these tests. Whatman No. 1 is suitable; better but much more expensive are the various types of spot-test papers offered by filter-paper manufacturers. The same test, using exactly similar technique and reagents, will appear different, depending upon the type and grade of filter paper used.

13. The Hand Spectroscope.—The hand spectroscope is a small portable instrument designed to show the most prominent lines in the spectrum of an element. In this course, it is used to help the student distinguish the alkaline earth elements. In use, the spectroscope should be clamped to a ring stand and pointed toward the flame of a Bunsen burner that is about 12 in. from it. The flame should be adjusted so that a sharp inner cone exists. The field of vision of the spectroscope should not include the inner cone of the burner, since this introduces extraneous lines. On looking through the spectroscope, one should see a black field cut by a yellow line. This is the sodium line and is due to traces of sodium in the air and to impurities in the burner tube. The focusing sleeve should then be pulled out until the edges of the sodium line are sharp and distinct. At this point, the spectroscope is in focus. One now introduces into the flame a cleaned platinum wire that has on it some of the metallic chloride. One sees in the spectroscope some sharp colored lines. If calcium chloride were the salt introduced, one would see a green line on one side of the sodium line and an orange-red line on the other (see Fig. 51). If the salt one is testing is not a chloride, it may be converted to a chloride by roasting in the flame and then running some concentrated hydrochloric acid over

it. The chlorides are used because the metallic chlorides of the alkaline earths are volatile, whereas other salts, like the sulfates, are not volatile in the Bunsen burner. The student should first work with known salts and thus become accustomed to the spectroscope and the spectra of the various elements before proceeding to the unknown.

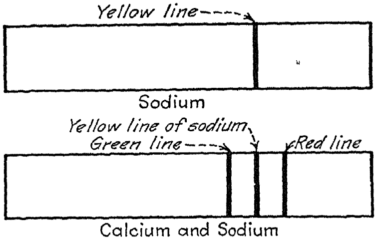


FIG. 51.—Schematic diagram of the spectra observed with a hand spectroscope.

14. Cleanliness.—Cleanliness, or the avoidance of contamination, is the keystone of successful analysis. When the use of water is mentioned in the experimental section, distilled water is to be employed. All apparatus should be **washed with tap water and rinsed with a small portion of distilled water.** The latter is not a cleaning agent but is used to remove the final traces of contaminants.

Apparatus that cannot be readily cleaned with a brush, soap, and water should be cleaned in cleaning solution, washed thoroughly with tap water, and finally rinsed with distilled water.

15. Precautions, Accidents.—The student should never forget that in the course in qualitative analysis, he is dealing with many toxic and corrosive substances. He should therefore handle materials with due respect for their properties. All accidents, no matter how minor, should be reported to the instructor immediately and first aid obtained.

CHAPTER XIII

CATION ANALYSIS

GROUP I CATIONS

SILVER, Ag

Silver occurs in Group 1*b* of the periodic table. Being comparatively unreactive, it is found in the native state and has consequently been known from earliest times. It does not displace hydrogen from acids or bases but is soluble in **oxidizing agents,** like nitric acid. Metallic silver is widely used in coins and common alloys.

The silver cation, monovalent, forms more insoluble compounds than any other known metal. The **nitrate** and **fluoride** are soluble in water; the **nitrite, acetate, sulfate,** and **chlorate** are only moderately soluble. **Chloride** ion precipitates white **silver chloride**, AgCl, insoluble in nitric acid and hot water. It is appreciably soluble, however, in a large excess of chloride ion with the formation of the complex **chloroargentate** (**argentichloride**) ions, $[AgCl_3]^{=}$ and $[AgCl_4]^{\equiv}$. Silver chloride is soluble in **ammonium hydroxide,** producing the complex **diamminosilver ion,** $[Ag(NH_3)_2]^+$, from which AgCl may be reprecipitated by acidification. The chloride decomposes upon exposure to bright sunlight and in the presence of organic matter. The former characteristic property, given also by the **bromide** and **iodide,** is the basis of present-day photography.

The **alkali cyanides,** KCN and NaCN, precipitate **silver cyanide,** AgCN, which is soluble in an excess of cyanide ion, forming the complex **cyanoargentate** (**argenticyanide**) ion, $[Ag(CN)_2]^-$. The **thiosulfate** ion, $S_2O_3^{=}$, converts silver chloride to the complex $[Ag_2(S_2O_3)_3]^{\equiv}$; a reaction given by all insoluble silver salts. This explains the use of "hypo," $Na_2S_2O_3$, in the "fixing" of photographic films. Since metallic silver is rather low in the electromotive series, it may be displaced from solution by most of the common metals. The recovery of silver from thiosulfate wash solutions used in photography is accomplished in this manner.

In neutral solution, ammonium hydroxide precipitates brown **silver oxide,** Ag_2O. Alkali carbonates yield white **silver carbonate,** Ag_2CO_3, which slowly decomposes into Ag_2O and CO_2 on standing. Among the

colored salts of silver are the pale yellow **bromide,** the yellow **iodide** and **phosphate,** and the orange **ferricyanide.** The black **sulfide,** Ag_2S, is soluble in hot, dilute nitric acid. The red **chromate,** Ag_2CrO_4, and the red or red-violet precipitate obtained with an ammoniacal solution of **p-dimethylamino benzalrhodanine** are used as qualitative tests for the detection of silver.

PRELIMINARY EXPERIMENTS

1. To 1 ml. of Ag^+ test solution in a micro test tube, add dilute HCl dropwise until precipitation is complete. Centrifuge the tube and contents, and filter. Place a small amount of the precipitate on a spot plate, and expose to strong light for a few minutes.

Place another portion of the silver chloride on a slide with a black background, and add ammonium hydroxide carefully until solution is complete. Acidify the diammino silver complex with dilute nitric acid. Treat some of the AgCl with a slight excess of sodium thiosulfate solution. Ascertain the solubility of AgCl in hot water.

2. Saturate 1 ml. of Ag^+ test solution with hydrogen sulfide.[1] Filter and discard the clear filtrate. Test the solubility of the precipitate in cold, dilute HCl. To a second portion of the precipitate, add dilute HNO_3, and heat carefully. Add more acid, if necessary, to effect complete solution.

3. Using a capillary medicine dropper, place a few drops of Ag^+ test solution on a piece of highly absorbent filter paper. From a second pipette, add an equal volume of 5% potassium chromate solution to the test spot.[2] Repeat the experiment, using a micro test tube and the same proportions of reagents.

4. To the slightly ammoniacal Ag^+ test solution on a spot plate, add a solution of *p*-dimethylamino benzalrhodanine (rhodanine reagent). Acidify with dilute nitric acid.

5. (*Optional*) *Detection of* Ag *in Coins or Valuable Alloys.*—Coins or other valuable alloys may be qualitatively tested for Ag without impairing the value or usefulness of the object. Rub the edge of a dime on a chip of unglazed porcelain. Moisten the line with a single drop of concentrated nitric acid, and warm carefully until the acid is completely evaporated. Carefully add a drop of the rhodanine reagent to the place where the line was traced. A violet-red colored zone is evidence of the presence of Ag in the coin.

[1] See Technique—Filtration and Centrifugation, p. 158–159; Precipitation and H_2S Generator, p. 157, 162.

[2] See Technique—Spot Tests, p. 164.

LEAD, Pb

Metallic lead falls in Group 4 of the periodic table. Although it is acted upon by all common acids and many weak organic acids, it is not readily dissolved, since many of the lead compounds thus formed are insoluble. Since the **nitrate** is one of the most soluble salts, nitric acid is generally used to dissolve the metal. Lead finds use in the manufacture of low melting alloys.

Lead forms divalent and tetravalent ions, the former being the more common and stable form. With chloride ion, white **lead chloride,** $PbCl_2$, is obtained that is soluble in an excess of chloride ion with the formation of the complex anion, $[PbCl_3]^-$. One gram of lead chloride is soluble in approximately 148 g. of H_2O at 0°C. and in approximately 30 g. of H_2O at 100°C. Therefore, lead can never be completely precipitated in Group I of the analytical scheme. Although the **sulfate** is very insoluble in water, it is soluble in ammonium acetate solution, because of the formation of slightly ionized **lead acetate,** $Pb(C_2H_3O_2)_2$. Lead ion gives a yellow precipitate with **chromates,** $PbCrO_4$, which is insoluble in acetic acid and water but soluble in nitric acid and alkalis.

Tetravalent lead, in the form of **lead dioxide,** PbO_2, is a good oxidizing agent. Hence benzidine, which yields a blue compound when treated with oxidizing agents, may be used to detect lead ion in the absence of other oxidizing agents. Hydrogen peroxide is used to convert divalent lead into lead dioxide. Alkali hydroxides precipitate white **lead hydroxide,** $Pb(OH)_2$, from Pb^{++} test solutions. The hydroxide is soluble in excess reagent, forming the anion, $[PbO_2]^=$.

PRELIMINARY EXPERIMENTS

1. Add dilute hydrochloric acid to 0.5 ml. of lead nitrate test solution; filter and wash the precipitate with a few drops of cold water. (Test a portion of the wash water with H_2S.) Treat a portion of the original precipitate with hot water, adding enough to ensure complete solution. Allow the solution to cool. Expose a small amount of the white lead chloride to strong light. Add a few drops of concentrated HCl to another sample of the precipitate.

2. Treat a few drops of the Pb^{++} test solution with dilute H_2SO_4. Test the solubility of the precipitate in hot water and in an excess of reagent. Add a few drops of glacial (concentrated) acetic acid and a few drops of a saturated solution of ammonium acetate to the lead sulfate, and warm gently. Add several drops of potassium chromate to the resulting solution.

3. Place a drop of Pb^{++} test solution on a filter paper, and add a mixture of equal volumes of dilute NH_4OH and of 3% hydrogen peroxide. Heat for a few minutes over a steam bath, and then add a drop of benzidine solution.

Mercury, Hg

Mercury, the only metallic element that is liquid at ordinary temperatures, occurs in Group 2 of the periodic table. It forms two cations, the monovalent mercurous, Hg_2^{++}, and the divalent mercuric, Hg^{++}. The former is studied in this group and the latter in Group II of the analytical scheme. The metal itself is difficult to oxidize because of its low position in the electromotive series. It is easily soluble in hot nitric acid, giving the **mercuric salt,** and in cold nitric acid, forming the **mercurous compound.** The **chloride,** called **calomel,** is used medicinally as a purgative and externally as a mild antiseptic.

The mercurous ion is stable to air but is converted to mercuric ion by strong oxidizing agents, like nitric acid. Mercurous ion gives a white precipitate with **chloride** ion, Hg_2Cl_2, which is insoluble in water and cold acids but is soluble, with oxidation to Hg^{++}, in hot concentrated HNO_3, H_2SO_4, and aqua regia. With ammonium hydroxide, mercurous chloride undergoes an oxidation-reduction reaction, giving a mixture of black metallic **mercury,** Hg, and **mercuric amido chloride,** $HgNH_2Cl$, which is white. With hydrogen sulfide, Hg_2^{++} forms black **mercuric sulfide,** HgS, and free **mercury** but no mercurous sulfide.

Green **mercurous iodide,** Hg_2I_2, is obtained by the action of the iodide ion on mercurous salts; chromate ion, $CrO_4^{=}$, gives a precipitate of red **mercurous chromate,** Hg_2CrO_4, in boiling solution. Mercurous ion reacts with stannous chloride solution, $SnCl_2$, to give a gray-black precipitate of elementary **mercury** and **mercurous chloride,** Hg_2Cl_2.

PRELIMINARY EXPERIMENTS

1. Add dilute HCl to 1 ml. of Hg_2^{++} test solution until precipitation is complete. Ascertain the solubility of the precipitate in hot water. Test a portion of the precipitate for any change on exposure to light. To some of the precipitate, add cold dilute nitric acid. Treat another portion with aqua regia.

2. Place the remainder of the precipitate on a spot plate, and carefully add ammonium hydroxide. Ascertain the solubility of the precipitate in warm aqua regia.

3. Pass H_2S through a few drops of Hg_2^{++} test solution. Add potassium iodide solution to another sample of test solution. To a third portion, add potassium chromate solution, and heat to boiling.

4. Suspend a few particles of mercurous chloride in water, and add a slight excess of stannous chloride solution.

ANALYSIS OF GROUP I CATIONS

Outline of Separations

The three cations of this group are precipitated as the sparingly soluble or insoluble chlorides. Lead chloride is separated from the group precipitate because of its complete solubility in hot water. Silver and mercurous chlorides are separated by their reaction with ammonium hydroxide, the former yielding a soluble complex ion, the latter a mixture of elementary mercury and mercuric amido chloride.

Analytical Procedure

1. Place 2 ml. of the neutral or slightly acid unknown solution in a micro test tube, and add HCl until precipitation is complete. Filter and wash the precipitate once with the least amount of cold water necessary. Reserve the combined filtrate and washings for the analysis of succeeding groups.

Note: If the solution is strongly acid, add NH_4OH until slight precipitate forms, then add a few drops of HNO_3 to clear the solution, before adding HCl.

2. Wash the precipitate once with hot water, and filter. Test for lead by placing a drop of the filtrate on a spot plate and adding an equal volume of potassium chromate solution.

A yellow precipitate, insoluble in dilute acetic acid, indicates **lead.**

Place another drop of the filtrate on a piece of filter paper, and add a few drops of a previously mixed solution of equal volumes of dilute NH_4OH and 3% H_2O_2. Heat the paper over a steam bath for a minute or two, and add a drop of benzidine solution to the wet spot.

A blue color proves the presence of **lead.**

If lead has been found, extract the precipitate exhaustively with hot water.

3. To the residue, from step 2, add ammonium hydroxide and stir. Filter and acidify a portion of the filtrate with dilute nitric acid.

A white precipitate indicates **silver.**

Place a drop of the filtrate on a spot plate, and add an equal volume of *p*-dimethylamino benzalrhodanine (rhodanine) solution. Acidify with HNO_3.

A red or red-violet precipitate confirms the presence of **silver.**

NOTE: In the presence of large amounts of Hg_2Cl_2 and very little AgCl, the latter may not dissolve in NH_4OH. The mercurous compound may be oxidized to the soluble mercuric salt by treating the black residue, after the NH_4OH treatment, with a mixture of 1 part of HCl to 3 parts of bromine water. The residue is finally washed with hot water and then treated with NH_4OH. The solution is then tested for Ag^+ as above.

If silver has been found, treat the precipitate thoroughly with NH_4OH until no further test for Ag^+ is obtained.

A black residue indicates the presence of **mercury.**

4. Add a few drops of aqua regia to the black precipitate, and warm until it is all dissolved. Add an excess of $SnCl_2$ solution.

A white precipitate turning gray confirms **mercury.**

ANALYTICAL TABLE I

Analysis of Group I

Unknown solution may contain the cations of all five analytical groups. Treat with HCl: white precipitate of $PbCl_2$, Hg_2Cl_2, and AgCl. Filter, reserve filtrate for subsequent group analyses (**1**).* Extract precipitate with hot H_2O (**2**).

Filtrate: Pb^{++}. Test portion with $CrO_4^{=}$ solution. Confirm with benzidine test (**2**).	**Precipitate:** AgCl, Hg_2Cl_2. Treat with NH_4OH, stir and filter (**3**).	
	Filtrate: $Ag(NH_3)_2^+$. Acidify portion with dilute HNO_3. Confirm Ag^+ with Rhodanine test (**3**).	**Precipitate:** Hg (black) and $HgNH_2Cl$ (white). Dissolve in aqua regia and test with $SnCl_2$ solution (**4**).

* Boldfaced numbers refer to steps in the procedure.

GROUP II CATIONS

Mercury, Hg

The divalent mercuric ion, Hg^{++}, forms a soluble **chloride.** With ammonium hydroxide, $HgCl_2$ yields a white precipitate of **mercuric amido chloride,** $HgNH_2Cl$. Hydrogen sulfide precipitates black **mercuric sulfide,** HgS, which is insoluble in water, dilute acids, concentrated hydrochloric acid, and ammonium polysulfide, $(NH_4)_2S_x$, but is soluble in aqua regia and, after long boiling, in concentrated nitric acid. Metals above mercury in the electromotive series displace the metal from its salts.

Alkali hydroxides precipitate yellow or red **mercuric oxide,** HgO, which is insoluble in an excess of reagent. Chromate ion precipitates orange **mercuric chromate,** $HgCrO_4$; the iodide ion precipitates red **mercuric iodide,** HgI_2, which is soluble in excess reagent with the formation of the colorless complex ion, $[HgI_4]^=$. **Stannous chloride** reacts with mercuric chloride to form first a white precipitate of Hg_2Cl_2, which changes to free **mercury** upon the addition of excess reagent. **Diphenyl carbazide,** added to an acid solution of Hg^{++} gives a violet or blue precipitate.

Mercuric sulfide, in ointment form, is used in the treatment of certain skin conditions. Amalgams are used in dentistry. Even slight concentrations of mercuric salts, taken internally, are violent poisons.

PRELIMINARY EXPERIMENTS

1. Acidify 1 ml. of Hg^{++} test solution with dilute HCl, and saturate with H_2S. Filter and wash the precipitate with warm water. Treat a portion of the black precipitate with aqua regia. Treat another portion with dilute HNO_3, and heat just to boiling. Repeat the experiment, boiling the mixture for several minutes. Ascertain the solubility of the precipitate in $(NH_4)_2S_x$.

2. Add ammonium hydroxide carefully to a few drops of $HgCl_2$ solution.

3. To the Hg^{++} test solution add very slowly a solution of stannous chloride until an excess has been added. Place a drop of Hg^{++} test solution on a filter paper that has been moistened with a solution of diphenyl carbazide in ethyl alcohol.

4. (*Optional*) Add either KOH or NaOH to a few drops of Hg^{++} test solution; then treat with an excess of reagent. To another portion of the test solution, add some KI solution. Ascertain the effect of excess reagent on the precipitate. Treat a third portion of Hg^{++} test solution with K_2CrO_4 solution.

LEAD, Pb

The sulfide ion precipitates black **lead sulfide,** PbS, from slightly acid, neutral, or weakly alkaline solutions. The sulfide is insoluble in water, dilute acids, bases, carbonates, and alkali sulfides. It is soluble in dilute nitric acid with the separation of elementary sulfur and in concentrated hydrochloric acid (see Lead, Group I).

PRELIMINARY EXPERIMENTS

1. Acidify 1 ml. of Pb^{++} test solution with dilute HCl, warm slightly, and saturate with H_2S. Filter and wash the precipitate, and

treat a portion of it with dilute HNO_3. Add several drops of dilute H_2SO_4 to the solution, and evaporate to dense fumes of SO_3. After cooling, pour the solution carefully into water. Filter the precipitate, and treat it with a warm, saturated solution of ammonium acetate that has been acidified with acetic acid. To the resulting solution, add K_2CrO_4 solution.

2. Repeat the benzidine test for lead as given under Group I.

Bismuth, Bi

Bismuth falls in Group 5 of the periodic table. The metal is rather inactive chemically, being below hydrogen but above mercury in the electromotive series. It is insoluble in hydrochloric acid and cold sulfuric acid but is soluble in nitric acid and hot sulfuric acid.

The cation usually exhibits a valence of 3. Most of the bismuth salts are insoluble. The soluble salts hydrolyze in water with the formation of the **hydroxy compounds.** Thus **bismuth trichloride,** $BiCl_3$, is converted to **bismuth dihydroxychloride,** $Bi(OH)_2Cl$, by water. This hydrolysis is inhibited by the presence of the corresponding free acid. The dihydroxychloride is therefore soluble in concentrated hydrochloric acid, reforming the trichloride. On long standing, the hydroxychloride is converted to the difficultly soluble **oxychloride,** $BiOCl$. The trichloride and dihydroxychloride form dark brown, insoluble **bismuth sulfide,** Bi_2S_3, with sulfide ion. This precipitate is insoluble in water and ammonium polysulfide but dissolves in hot hydrochloric acid and in dilute nitric acid.

Alkali hydroxides precipitate white **bismuth hydroxide,** $Bi(OH)_3$, which is insoluble in water and excess reagent but is soluble in acids. Alkali stannites, like **sodium stannite,** Na_2SnO_2, added to bismuth compounds, precipitate black, metallic **bismuth. Cinchonine** reagent, in faintly acid solution, gives an orange precipitate with bismuth ion.

PRELIMINARY EXPERIMENTS

1. Saturate 1 ml. of an acid solution of Bi^{+++} with H_2S. Filter and wash the precipitate with water. Ascertain the solubility of the sulfide in ammonium polysulfide. Treat some of the precipitate with dilute HNO_3, and boil for a short time. Add a few drops of concentrated H_2SO_4 to the solution, and evaporate to fumes of sulfur trioxide. After cooling, pour the solution into cold water, and add excess NH_4OH. Dissolve a small portion of the precipitate in concentrated HCl. Treat several drops of the solution with cold water. Test the solubility of the precipitate in an excess of HCl.

2. Dissolve some $Bi(OH)_3$ in the least amount of HCl necessary. Add 1 drop of the solution to filter paper previously impregnated with 1 drop of concentrated NH_4OH. Add 1 drop of freshly prepared sodium stannite solution to the mixture on the paper.

3. Place a drop of the faintly acid Bi^{+++} test solution on filter paper that has been previously treated with a drop of cinchonine reagent.

Copper, Cu

Copper is placed in Group 1 of the periodic table. The element resembles mercury in some of its reactions. It is soluble in oxidizing acids like nitric acid and hot, concentrated sulfuric acid. Since it is above both mercury and silver in the electromotive series, it may displace both these cations from their compounds. Copper is an excellent conductor of heat and electricity. Because copper salts are poisonous, they are often used commercially as fungicides.

Copper forms two cations, the monovalent cuprous and the divalent cupric ions. The latter are more common analytically and are therefore the only type considered. **Cupric** salts are either blue or green in dilute aqueous solution; in the anhydrous state, they are usually either white or yellow. Ammonium hydroxide, in small amounts, precipitates **basic salts,** like $Cu_2(OH)_2SO_4$, which are extremely soluble in an excess of reagent, forming a deep blue solution of the **tetrammino-cupric** ion, $[Cu(NH_3)_4]^{++}$. Alkali cyanides convert this ion to the colorless **cuprocyanide** ion, $Cu(CN)_3^-$. This ion is only very slightly dissociated and does not give a precipitate of **copper sulfide** on treatment with hydrogen sulfide.

From solutions of Cu^{++}, hydrogen sulfide precipitates black **cupric sulfide,** CuS, which is insoluble in dilute, nonoxidizing acids and slightly soluble in ammonium polysulfide, $(NH_4)_2S_x$. The sulfide is soluble in hot, dilute nitric acid. It is also soluble in alkali cyanides, the complex **cuprocyanide** ion being formed with the latter reagent. Sodium and potassium hydroxides precipitate blue **cupric hydroxide,** $Cu(OH)_2$, from Cu^{++} solutions. The hydroxide is converted to brown-black **cupric oxide,** CuO, on standing or boiling.

Potassium ferrocyanide, $K_4Fe(CN)_6$, precipitates red-brown **cupric ferrocyanide,** $Cu_2Fe(CN)_6$, insoluble in dilute acids but soluble in ammonium hydroxide. A green precipitate is formed in the Cu^{++} spot test with α-**benzoinoxime.**

Preliminary Experiments

1. Saturate 1 ml. of a warm, acidified solution of Cu^{++} with H_2S. Filter and wash the precipitate with hot water. Boil a portion of the

precipitate with dilute HNO_3. Cool the solution, add NaOH, and heat.

2. Treat another portion of the test solution carefully with NH_4OH; then add an excess of reagent. To a few drops of the ammoniacal solution, add KCN dropwise until the blue color just disappears, then add 2 drops in excess. (**CAUTION:** Never acidify cyanide solutions.) Saturate the colorless solution with H_2S.

3. Acidify a portion of the test solution with dilute acetic acid, and then add $K_4Fe(CN)_6$ solution. Test the solubility of the precipitate in both NH_4OH and dilute HNO_3.

4. Place a drop of the Cu^{++} test solution on a piece of filter paper, and add an equal volume of a 5% solution of α-benzoinoxime to the wet spot. Hold the paper over an open bottle of NH_4OH for several minutes.

5. (*Optional*) Immerse a penny in a small volume of concentrated HNO_3 for about 5 sec. Cautiously make the solution strongly ammoniacal.

Cadmium, Cd

Cadmium is found in Group 2 of the periodic table. It is moderately active, being a little above hydrogen in the electromotive series. It is readily soluble in nitric acid and dissolves slowly in hydrochloric acid and sulfuric acid. Cadmium burns in air to form the brown **oxide,** CdO. The metal is used extensively in the manufacture of yellow paint and also finds great use in the manufacture of a number of valuable low-melting alloys.

The cation is divalent in all its compounds. Sulfide ion precipitates yellow or orange **cadmium sulfide,** CdS, which is insoluble in water, ammonium hydroxide, ammonium polysulfide, and alkali cyanides. The sulfide is soluble in hydrochloric acid, nitric acid, and hot, dilute sulfuric acid. Alkali hydroxides yield white **cadmium hydroxide,** $Cd(OH)_2$, which is insoluble in excess reagent but is soluble in acids. Ammonium hydroxide also precipitates $Cd(OH)_2$, which is soluble in an excess of reagent with the formation of the colorless $[\mathbf{Cd(NH_3)_4}]^{++}$ ion. This ion is converted to the colorless **cadmocyanide (tetracyanocadmate)** ion, $[Cd(CN)_4]^{=}$, upon reaction with alkali cyanides. However, this ion dissociates to some extent, furnishing sufficient cadmium ions to precipitate **cadmium sulfide** with hydrogen sulfide.

Potassium ferrocyanide forms white **cadmium ferrocyanide,** $Cd_2Fe(CN)_6$, with Cd^{++} test solutions. A yellow precipitate or solution is obtained upon the reaction of cadmium solutions with **thiosinamine.**

PRELIMINARY EXPERIMENTS

1. Saturate 1 ml. of Cd^{++} test solution, acidified with dilute acetic acid, with H_2S. Heat to boiling, filter, and wash the precipitate. Ascertain the solubility of the precipitate in hot, dilute HNO_3. Make the resulting solution alkaline with NaOH.

2. Repeat the preceding experiment, strongly acidifying the test solution with HCl.

3. Add NH_4OH carefully to another portion of test solution, using enough excess to redissolve the precipitate that first forms. To the solution, add KCN solution, and then saturate with H_2S. **(CAUTION.)**

4. Add some $K_4Fe(CN)_6$ solution to a few drops of the test solution.

5. Make a few drops of Cd^{++} test solution alkaline with NaOH. Add a small crystal of thiosinamine, and warm.

Arsenic, As

Arsenic, which falls in Group 5 of the periodic table, exists in several allotropic modifications; the most usual form is steel-gray in color and has a metallic luster. Since it is in Group 5, it is very similar to phosphorus and forms corresponding series of salts; **arsenites,** AsO_2^-, and **arsenates,** $AsO_4^{\equiv}$. It is, however, more metallic than phosphorus and therefore forms simple cations, trivalent **arsenous** and pentavalent **arsenic.**

Arsenic dissolves readily in nitric acid. It is insoluble in cold, concentrated hydrochloric acid and cold, dilute sulfuric acid. The metal, on heating in air, forms **arsenic trioxide,** As_2O_3, with the simultaneous production of a garlic odor. The vapors are poisonous. Arsenic compounds have been known to man since ancient times. In modern times, they are used extensively as poisons in fungicides, wood preservatives, and poison gases like Lewisite. Organic arsenic compounds are also used medicinally as spirocheticidal and trypanocidal agents.

The **trioxide** is only very slightly soluble in water but dissolves readily in hydrochloric acid with the formation of the **arsenous ion,** As^{+++}. With alkali hydroxides, the oxide forms the **arsenite ion,** AsO_2^-. The **pentoxide,** As_2O_5, is easily soluble in water, forming **arsenic acid,** H_3AsO_4; with alkalis it produces **arsenates.**

Hydrogen sulfide readily precipitates the yellow **trisulfide** from $0.3N$ acid solutions of arsenous ion. Under the same conditions, however, **arsenic pentasulfide** is not precipitated from arsenate solutions, only the **trisulfide** being obtained after long treatment with hydrogen sulfide. The pentasulfide may be precipitated from a cold solution

containing a large excess of concentrated hydrochloric acid. A mixture of the two sulfides is precipitated when a hot solution of arsenate ion in concentrated hydrochloric acid is treated with hydrogen sulfide. In neutral or alkaline solution, soluble **thio salts** are obtained on treatment with hydrogen sulfide. Similar salts are formed on treatment of the sulfides with alkali sulfides and polysulfides. Arsenic trisulfide, with ammonium sulfide, $(NH_4)_2S$, gives the **thioarsenite** ion, $AsS_3^{\equiv}$. With ammonium polysulfide, $(NH_4)_2S_x$, oxidation and solution takes place with the formation of the **thioarsenate** ion, $AsS_4^{\equiv}$. Arsenic pentasulfide yields only the **thioarsenate** ion under the same conditions. Neutralization of the solutions produces the **trisulfide** from the thioarsenite and the **pentasulfide** from the thioarsenate. Arsenic pentasulfide is soluble in ammoniacal H_2O_2 with the formation of $AsO_4^{\equiv}$.

Neutral solutions of arsenite ion yield, with silver nitrate, yellow **silver arsenite,** Ag_3AsO_3, which is soluble in dilute acids and ammonium hydroxide. Arsenates under the same conditions form chocolate brown **silver arsenate,** Ag_3AsO_4, soluble in the same reagents. Treatment of arsenites with stannous chloride in concentrated hydrochloric acid solution produces a brown to black precipitate of metallic **arsenic.** This is the **Bettendorf test.**

Reduction of arsenic compounds with acids and active metals produces **arsine,** AsH_3. This gas is used to identify arsenic in several ways. One of the most important, the **Gutzeit test,** depends upon the reaction of arsine with a crystal of silver nitrate; a yellow coloration of $AsAg_3 \cdot 3AgNO_3$ is obtained that rapidly turns to black, metallic silver. Treatment of trivalent arsenic compounds with hydrochloric acid and a strip of bright copper foil leads to the deposition of a gray film of Cu_5As_2 on the surface of the metal. This is the **Reinsch test.**

Arsenates give a white precipitate of **magnesium ammonium arsenate,** $MgNH_4AsO_4$, with magnesia mixture. **Arsenites** do not react. With ammonium molybdate, $(NH_4)_2MoO_4$, arsenates form a yellow precipitate of **ammonium arsenomolybdate,** $(NH_4)_3AsO_4 \cdot 12MoO_3$. Sodium thiosulfate precipitates **arsenic pentasulfide** from faintly acid solution.

PRELIMINARY EXPERIMENTS

1. Make 1 ml. of As^{+++} test solution $0.3N$ with HCl. Saturate the solution with H_2S at room temperature.

   NOTE: To make a solution $0.3N$, neutralize the solution, and then add the amount of acid needed to bring the solution to $0.3N$.

2. Repeat the experiment, using pentavalent arsenic test solution. Repeat, using a hot solution.

3. Make 1 ml. of As^{+5} test solution $0.5N$ with HCl, heat the solution to boiling, and saturate with H_2S. Filter and wash the precipitate. Add $(NH_4)_2S_x$ solution to one portion of the precipitate. Save the rest for step 4. Neutralize the solution with dilute HCl and filter. Add concentrated HCl to the precipitate and heat to boiling. Ascertain the solubility of the precipitate in NH_4OH and NaOH.

4. Place a small amount of As_2S_5 precipitate in a crucible, and dissolve it in the least volume of ammoniacal H_2O_2 required. Add magnesia mixture, evaporate to dryness, and ignite. Cool the crucible, and moisten the residue with a few drops of Bettendorf's reagent.

5. Treat a few drops of arsenate test solution with $AgNO_3$ solution. Repeat, using a neutral arsenite test solution. Add magnesia mixture to several drops of both arsenate and arsenite test solutions. Treat separate portions of the test solutions with a hot HNO_3 solution of ammonium molybdate.

6. *Gutzeit Test.*—In a test tube, place a small amount of arsenic test solution; add a stick of As-free Zn and a small volume of dilute H_2SO_4. Place a wad of cotton in the mouth of the tube, and fold a piece of filter paper with a crystal of $AgNO_3$ over the mouth of the tube. Run the test in conjunction with a blank, using Zn and acid alone.

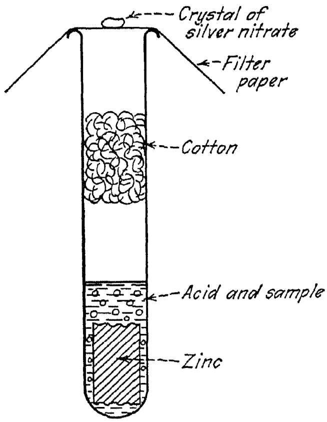


FIG. 52.—Gutzeit test.

7. Place a piece of copper foil in a test tube, add a few drops of an HCl solution of As^{+++}, and warm.

8. (*Optional*) On a silver coin previously cleaned with HNO_3, place a drop of As^{+++} test solution acidified with HCl. Touch the coin and liquid with a stick of As-free zinc. After the black stain has developed, remove the zinc, and wash the coin with water. Ascertain the solubility of the stain in NaOBr.

ANTIMONY, Sb

Antimony, which falls in Group 5 of the periodic table, is a rather unreactive element. The metal has a bright silvery luster and does not tarnish readily in dry air. It has been known from early times. At present, it is used chiefly in alloys, storage-battery plates, and medicinals.

Since it is in the same family as arsenic, it forms cations exhibiting valences of 3 and 5, and the anions $SbO_3^{\equiv}$ and $SbO_4^{\equiv}$. However, having a higher atomic number than arsenic, it is more metallic in character. The trivalent ion is slightly basic in its reactions.

Trivalent antimony salts, like the **chloride,** are readily hydrolyzed in water, precipitating white **hydroxy salts** like the **dihydroxy chloride,** $Sb(OH)_2Cl$. This precipitate, when fresh, is readily soluble in concentrated mineral acids, tartaric, citric, and oxalic acids but not in acetic acid. Alkalis and alkali carbonates precipitate white $Sb(OH)_3$, which is soluble in acids or an excess of strong alkali.

From **trivalent antimony** solutions or from freshly precipitated $Sb(OH)_2Cl$, sulfide ion precipitates orange-red **antimony trisulfide,** Sb_2S_3. The sulfide is insoluble in dilute, nonoxidizing acids but is soluble in concentrated hydrochloric acid. It is also soluble in ammonium polysulfide with oxidation and the formation of a soluble **thio derivative** of **antimonic acid,** $SbS_4^{\equiv}$.

Pentavalent antimony ion forms, with sulfide ion, orange **antimony pentasulfide,** Sb_2S_5, which is soluble in ammonium polysulfide with the formation of the **thioantimonate** ion. When the solution is treated with dilute hydrochloric acid, Sb_2S_4 is precipitated; this is soluble in concentrated hydrochloric acid.

Antimony is below hydrogen in the electromotive series and is therefore displaced from its salts by many metals. This fact is utilized in the **"couple test,"** in which bimetallic couples like silver and tin, copper and tin, zinc and silver, and platinum and zinc are used. Antimony ion, in contact with such a couple, is plated out on the nobler metal. The metal, unlike arsenic, is only slowly soluble in **sodium hypobromite** solution. With sodium thiosulfate in hot, slightly acid solution, antimony ion precipitates as **"antimony cinnabar,"** $SbOS_2$. **Rhodamine B** gives a violet color with pentavalent antimony solutions.

PRELIMINARY EXPERIMENTS

1. Make 1 ml. of Sb^{+++} test solution $0.3N$ with HCl. Saturate with H_2S; filter and wash the precipitate with hot water. Treat a portion of the precipitate with $(NH_4)_2S_x$, using enough to effect complete solution. Acidify the resulting solution with dilute HCl. Treat the precipitate with concentrated HCl. Warm to effect solution and to expel excess H_2S. Dilute the solution with an equal volume of water, and pass in H_2S.

2. Place a few drops of the acid test solution on a silver coin. Touch the liquid and metal with a piece of tin. Wash the spot with water, and add a drop of NaOBr solution.

3. Add H_2O to a few drops of Sb^{+++} test solution until a precipitate forms. Treat the suspended solid with concentrated HCl.

4. *Antimony Cinnabar Test.*—Add dilute NH_4OH solution to the test solution until precipitation just begins. Heat to boiling, and add a few crystals of $Na_2S_2O_3$.

5. To a portion of the test solution add a small amount of solid $NaNO_2$ or KNO_2. Shake until the evolution of gas ceases. Fill one of the depressions in a spot plate almost to the top with dilute rhodamine B solution. To this add 2 drops of the oxidized antimony solution.

Tin, Sn

Tin is a soft, malleable metal, known since prehistoric times. It is placed in Group 4 of the periodic table. Being just above hydrogen in the electromotive series, it displaces the latter from most acids. However, with nitric acid, it yields white, insoluble **metastannic acid.** Tin is used chiefly in the manufacture of alloys—solder, brass, bronze, type metal, Wood's metal—and in plating.

Tin forms divalent (**stannous**) and tetravalent (**stannic**) cations and the corresponding anions, **stannite,** $SnO_2^{=}$, and **stannate,** $SnO_3^{=}$. The stannous ion is more basic in its reactions than the stannic form. The latter form is also more stable, stannous ion undergoing oxidation in air to the higher valence state.

Alkalis and alkali carbonates precipitate white **stannous hydroxide,** $Sn(OH)_2$, which is soluble in excess alkali with the formation of the **metastannite** ion, $(HSnO_2)^-$. On standing, solutions of stannite ion slowly decompose into brown **stannous oxide,** SnO, and metallic **tin.** Stannous salts hydrolyze in water, stannous chloride forming first white **hydroxychloride,** Sn(OH)Cl, and then the **hydroxide,** with an excess of water. The addition of hydrochloric acid and metallic tin to stannous ion solutions prevents hydrolysis of the aqueous solution and oxidation to the stannic ion.

In not too acid solution, sulfide ion precipitates brown **stannous sulfide,** SnS, from stannous ion solutions. The sulfide is soluble in concentrated hydrochloric acid but is insoluble in ammonium hydroxide. With ammonium polysulfide, stannous sulfide dissolves, with oxidation, to form the **thiostannate** ion, $SnS_3^{=}$. Acids precipitate yellow **stannic sulfide,** SnS_2, from this solution. From solutions of stannic ion, sulfide ion precipitates yellow **stannic sulfide** slowly. It is soluble in hydrochloric acid, ammonium polysulfide, and sodium and potassium hydroxides.

Stannous and stannite ions are excellent reducing agents. With mercuric chloride, **stannous chloride** forms white **mercurous chloride** and then black, metallic **mercury**, with an excess of reagent. Stannic chloride does not react with mercuric chloride. **Alkali stannites**, freshly prepared, reduce bismuth ion to metallic bismuth. Stannous ion produces a violet color with **cacotheline.** Stannic compounds must first be reduced with magnesium and acid before applying the test.

PRELIMINARY EXPERIMENTS

1. Pass H_2S into a faintly acid test solution of Sn^{++} until precipitation is complete. Filter and wash the precipitate. Treat some of the precipitate with orange $(NH_4)_2S_x$ solution, warming to 60°C., if necessary. Acidify the solution with dilute HCl. Add concentrated HCl to another portion of the precipitate, and heat. Saturate the solution with H_2S.

2. Repeat all the foregoing, using Sn^{++++} test solution.

3. To several drops of $SnCl_2$, in a test tube, add a few drops of $HgCl_2$, followed by an excess of reagent. Repeat the test with $SnCl_4$.

4. Place a 2-cm. strip of magnesium ribbon into 1 ml. of an acid solution of $SnCl_4$. Add more acid, if necessary, to dissolve the metal completely. Filter rapidly, and test the filtrate with $HgCl_2$.

5. Place 1 or 2 drops of an acid solution of Sn^{++} on a piece of filter paper. Treat the wet spot with an equal volume of cacotheline solution.

ANALYSIS OF GROUP II CATIONS

Outline of Separations

The cations of Group II precipitate as sulfides in acid concentrations of 0.3*N* with respect to hydrochloric acid, when treated with hydrogen sulfide. At this pH, the sulfide ion concentration is sufficiently repressed to prevent precipitation of the Group III cations. The cations are further divided into two subgroups, *A* and *B*, on the basis of their solubility in ammonium polysulfide. Subgroup *A*, the insoluble sulfides, are mercuric mercury, lead, bismuth, copper, and cadmium; subgroup *B*, the soluble sulfides, are arsenic, antimony, and tin.

The sulfides of subgroup *A* are separated as follows: mercuric sulfide by its insolubility in nitric acid; lead by the insolubility of its sulfate; bismuth as the insoluble hydroxide. Copper and cadmium are converted to the cyanide complexes and separated with hydrogen sulfide, the former giving no precipitate because of the stability of the cuprocyanide ion.

The sulfides of subgroup *B* are reprecipitated with hydrochloric acid. Arsenic is separated because of the insolubility of its sulfide in concentrated hydrochloric acid. Antimony and tin are detected in the presence of each other.

Analytical Procedure

The unknown may be the filtrate from Group I or an unknown solution containing the mixed cations of Group II and subsequent groups.

1. In either case, adjust the acidity to 0.3*N*, and precipitate the sulfides as follows. Neutralize the unknown with NH_4OH, and then make faintly acid by adding 1 drop of very dilute HCl. To 3 ml. of this solution add 5 drops of 6*N* HCl, heat the solution to boiling and saturate with H_2S. Cool, dilute to 5 ml. with distilled water, and pass in H_2S again until precipitation is complete.

2. Filter and wash the precipitate with hot water. Save the precipitate for step 3. Combine the filtrate and washings, make strongly acid with HCl, and boil till all the H_2S is expelled. Discard the residue, and save the filtrate for the analysis of Groups III, IV, and V.

Note: It is often advisable to wash the precipitate with 0.3*N* HCl, which has been saturated with H_2S.

3. Extract the precipitate from step 2 once or twice with small portions of fresh ammonium polysulfide heated to about 60°C.[1] Filter and reserve the filtrate for the analysis of subgroup *B* (step 11).

subgroup *A*

4. Heat the precipitate remaining from the preceding treatment almost to boiling with about 0.5 ml. of dilute nitric acid. Filter and wash the precipitate with cold water. Save the filtrate for step 6.

5. Dissolve a portion of the black precipitate of HgS from step 4 in aqua regia. Evaporate nearly to dryness (moist solid) to expel the excess reagent. Dilute with several drops of water, and add a slight excess of $SnCl_2$ solution.

White precipitate turning gray-black indicates **mercury.**

To a second portion of the precipitate, add about 0.5 ml. of bromine water, and heat on a water bath until the solution becomes colorless. Repeat with another 0.5 ml. of bromine water. Add 5 drops of concentrated H_2SO_4 to this solution, and evaporate to copious fumes of SO_3 (use a crucible). Cool, dilute the solution with several drops of

[1] See Technique, Extraction, p. 161.

water, and add an excess of solid sodium acetate. Treat with several drops of diphenyl carbazide solution and 1 ml. of amyl alcohol.

Deep blue coloration in the amyl alcohol layer proves presence of **mercury.**

NOTE: The success of this test depends upon the complete conversion of the mercuric sulfide to the bromide and upon the subsequent elimination of all of the bromide ion as HBr. Mercuric halides, because of their slight ionization, give only very weak tests with diphenyl carbazide. It is advisable always to run a parallel control experiment with known HgS.

6. Boil the filtrate from step 4 with about 0.5 ml. of concentrated H_2SO_4 until dense white fumes of SO_3 are given off. Cool the solution, and pour cautiously into 1 to 2 ml. of cold water. Filter and save the filtrate for step 7.

NOTE: If considerable amounts of bismuth are present, some $(BiO)_2S_2O_7 \cdot 3H_2O$ may also be precipitated which may be recognized by its coarser crystals. To correct this condition, treat the precipitate with 1 ml. of dilute HCl and 0.5 ml. of concentrated H_2SO_4, heat to copious fumes of SO_3, and proceed as before.

Heat the precipitate of $PbSO_4$ almost to boiling with about 0.5 ml. of a saturated solution of ammonium acetate, acidified with $HC_2H_3O_2$. Treat a portion of this solution with K_2CrO_4 solution.

Yellow precipitate proves **lead** present.

NOTE: Use a micro slide or test tube for this experiment.

7. To the filtrate from step 6, add NH_4OH until the solution is strongly ammoniacal. Filter, and reserve the filtrate for step 8. Dissolve the precipitate in the least volume of HCl required. Place a drop of the solution on a piece of filter paper, and add a drop of concentrated NH_4OH. Treat the precipitate with a freshly prepared solution of sodium stannite.

Black precipitate proves metallic **bismuth.**

Add a drop of the acid solution to a piece of filter paper that has been previously treated with an equal volume of cinchonine reagent.

Orange precipitate proves presence of **bismuth.**

8. If the filtrate from step 7 has a deep blue color, the presence of copper is indicated. Neutralize a drop of the solution with acetic acid, and add $K_4Fe(CN)_6$ solution.

Red precipitate of $Cu_2Fe(CN)_6$ indicates **copper.**

NOTE: This test is much more sensitive than the blue complex obtained with ammonium hydroxide.

Place a drop of the blue solution on a piece of filter paper and add α-benzoinoxime to the wet spot. Hold over an open bottle of NH_4OH.

Green spot confirms **copper.**

9. If copper has been found to be present, carefully add KCN solution to the remainder of the blue ammoniacal solution from step 7 until the color is completely discharged, and proceed as in step 10. If no copper was found (colorless solution), make the solution faintly acid with H_2SO_4, and proceed as in step 10.

10. Saturate the colorless solution with H_2S.

Yellow precipitate of CdS indicates **cadmium.**

NOTE: If a dark precipitate is obtained at this point, it indicates that the previous separations have been incomplete. In order to remove the traces of other Group II*A* metals present, wash the precipitate thoroughly, treat with H_2SO_4 (1 part $6N$ H_2SO_4 to 4 parts H_2O), and boil gently. Filter, make the filtrate ammoniacal, and filter again. Saturate the filtrate with H_2S. If cadmium was present in the original precipitate, yellow CdS will form.

Filter the precipitate, and digest with several drops of HNO_3. Heat to expel excess H_2S. Cool, and filter if necessary. Make the solution alkaline with NaOH, and add a crystal of thiosinamine.

Yellow solution or precipitate proves **cadmium.**

SUBGROUP *B*

11. To the filtrate from step 3, add HCl until the solution is distinctly acid.

NOTE: If none of this group is present, the precipitate will be white. Often a tannish precipitate is obtained in the absence of Group II*B* metals. This is due to the presence of minute amounts of CuS. CuS is slightly soluble in $(NH_4)_2S_x$.

Filter and discard the filtrate. Add 1 ml. of concentrated HCl to the precipitate, and heat in boiling water for about 5 min., filter, and save the precipitate for step 14.

NOTE: Arsenic sulfide is not soluble in HCl but may be converted to the volatile trichloride upon boiling with acid. Therefore, the temperature in the preceding treatment must not be more than 100°C.

12. Evaporate the filtrate to about one-half the original volume to remove excess H_2S. Place a drop of the concentrated solution on silver coin, and touch the drop with a piece of tin.

Jet black spot, forming almost immediately, indicates **antimony.**

Dilute 2 drops of the solution with an equal volume of water. Add a small amount of solid $NaNO_2$ or KNO_2.

NOTE: The dilution should not be carried to the point of precipitation. If precipitation does occur, add dilute HCl until the precipitate just redissolves. Nitrite is added at this point to oxidize the antimony to the pentavalent state. The previous treatment of the mixed sulfides with concentrated HCl reduced the antimony to the trivalent state. The following test *must* be carried out with antimony in the oxidized state.

Shake the tube and contents until no further evolution of gas takes place. Fill one of the depressions in a spot plate almost to the rim with rhodamine B solution. Add 2 drops of the oxidized antimony solution.

Color change to violet indicates **antimony.**

NOTE: It is best to perform this test in comparison with a control. Use a drop or two of pentavalent antimony solution in order to observe the proper color change. If either of the tests is ambiguous or inconclusive, perform either the hydrolysis test or the "antimony cinnabar" test as given in the preliminary experiments.

13. Treat the remainder of the solution with a 1- to 1.5-cm. strip of magnesium ribbon to reduce the stannic ion to the stannous condition, and filter rapidly. Divide the filtrate into two portions.

NOTE: Use excess magnesium, if necessary. The reaction should be fairly vigorous. It is important that all the metal be permitted to dissolve before filtering. Add more acid, if necessary, to effect complete solution.

Place one portion of the solution in a test tube and add $HgCl_2$ solution.

White precipitate turning gray indicates **tin.**

Place 1 or 2 drops of the second portion of the solution on filter paper, and treat with an equal volume of cacotheline solution.

Violet color proves the presence of **tin.**

14. Dissolve part of the precipitate of As_2S_5, obtained in step 11. in warm NH_4OH to which have been added several drops of H_2O_2.

NOTE: If no appreciable solution takes place, the residue is probably elementary sulfur and may be discarded.

Place the solution in a crucible, add magnesia mixture, evaporate to dryness, and ignite. Allow the solid to cool, and add several drops of Bettendorf's reagent.

Brown coloration, gradually deepening, indicates **arsenic.**

The rest of the precipitate is dissolved in aqua regia and the solution

ANALYTICAL TABLE II

Analysis of Group II

Filtrate from Group I separation may contain Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, As^{+++}, As^{+++++}, Sb^{+++}, Sb^{+++++}, Sn^{++}, and Sn^{++++}, as well as the cations of Groups III, IV, and V. Adjust the acidity as directed, and saturate with H_2S (**1**): HgS (black), PbS (black), Bi_2S_3 (brown-black), CuS (black) CdS (yellow), As_2S_3 (yellow), As_2S_5 (yellow), Sb_2S_3 (orange), Sb_2S_5 (orange), SnS (brown), SnS_2 (yellow). Filter, acidify with HCl, boil until H_2S is expelled, and reserve the filtrate for subsequent group analyses (**2**). Extract precipita e with warm solution (**3**).

Precipitate: HgS, PbS, Bi_2S_3, CuS, CdS. Proceed as in Analytical Table III.	**Filtrate:** $AsS_4^{\equiv}$, $SbS_4^{\equiv}$, $SnS_3^{=}$. Proceed as in Analytical Table IV.

ANALYTICAL TABLE III

Analysis of Group IIA

Heat residue from Table II with HNO_3 to boiling and filter (**4**).

<table>
<tr><td rowspan="3">Precipitate: HgS. Dissolve portion in aqua regia, expel excess reagent and test for Hg^{++} with $SnCl_2$ solution. Confirm with diphenylcarbazide test (5).</td><td colspan="3">Filtrate: Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}. Boil with concentrated H_2SO_4 to fumes of SO_3, cool and dilute with H_2O. Filter (6).</td></tr>
<tr><td rowspan="2">Precipitate: $PbSO_4$ (white). Dissolve in $NH_4C_2H_3O_2$-$HC_2H_3O_2$ solution and test for Pb^{++} with $CrO_4^{=}$ solution (6).</td><td colspan="2">Filtrate: Bi^{+++}, Cu^{++}, Cd^{++}. Make strongly ammoniacal and filter (7).</td></tr>
<tr><td>Precipitate: $Bi(OH)_3$ (white). Dissolve in HCl, reprecipitate on the filter paper with NH_4OH and test with fresh Na_2SnO_2 solution. Confirm with cinchonine test (7).</td><td>Filtrate: $Cu(NH_3)_4^{++}$ (deep blue) and $Cd(NH_3)_4^{++}$ (colorless). Neutralize a portion with $HC_2H_3O_2$ and test for Cu^{++} with $K_4Fe(CN)_6$ solution. Confirm with α-benzoinoxime (8). If Cu^{++} present, treat another portion with KCN until colorless (9). Saturate with H_2S to test for Cd^{++}. Confirm with thiosinamine test (10).</td></tr>
</table>

evaporated to dryness. The residue is taken up in a small volume of water made slightly acid with acetic acid and treated with a small amount of solid sodium acetate and $AgNO_3$ solution added.

Chocolate brown precipitate of Ag_3AsO_4 proves **arsenic.**

Note: The test should be carried out on a spot plate. The precipitate should form immediately. Formation of a brown precipitate after

several minutes means that the silver nitrate has been converted to by H_2S fumes in the laboratory.

ANALYTICAL TABLE IV

Analysis of Group II*B*

Treat filtrate from Analytical Table II with dilute HCl until distinctly acidic, and filter. Precipitate may contain As_2S_5, Sb_2S_4, SnS_2. Heat the precipitate with concd. HCl, and filter (**11**).

Precipitate: As_2S_5. Dissolve a portion in warm NH_4OH-H_2O_2 solution. Treat with magnesia mixture, evaporate to dryness, and ignite. Test with Bettendorf's reagent. Dissolve another portion of the As_2S_5 in aqua regia. Evaporate to dryness. Take up in H_2O, make slightly acid with $HC_2H_3O_2$, and add $AgNO_3$ (**14**).

Filtrate: Sb^{+++}, Sn^{++++}. Evaporate and test portion for Sb^{+++} with Sn-Ag couple. Confirm by oxidation to pentavalent state, and test with rhodamine B solution (**12**). Reduce remainder of solution with Mg, filter and test portion with $HgCl_2$ solution. Confirm Sn^{++} with cacotheline test (**13**).

GROUP III CATIONS

Aluminum, Al

Aluminum, a silvery, fairly soft metal, was first isolated in the early part of the nineteenth century, notwithstanding the fact that its compounds comprise a large part of the earth's crust. For a long time it was as expensive as platinum, but with the advent of the Hall electrolytic process, the price quickly dropped. The metal is an excellent conductor of heat and electricity. It is very light and is used extensively in the manufacture of strong, lightweight alloys, cooking utensils, and automobile parts. Duralumin is an important alloy used in construction where lightness and strength are required. Aluminum is placed in Group 3 of the periodic table.

When pure, **aluminum** is only very slightly oxidized in air. It is soluble in hot, concentrated sulfuric acid with the evolution of sulfur dioxide. The metal dissolves in hydrochloric acid with the evolution of hydrogen, as might be expected from the position of aluminum in the electromotive series. When treated with nitric acid, the metal becomes "passive" and so unreactive that the concentrated acid can be shipped in aluminum drums. Aluminum reacts with alkalis, liberating hydrogen and forming the amphoteric **meta-aluminate** ion, AlO_2^-.

The cation exists only in the trivalent form. Its salts are generally colorless. Many aluminum compounds hydrolyze in aqueous solution. The **sulfide,** Al_2S_3, is unstable in solution, and the cation is therefore always precipitated as the **hydroxide,** $Al(OH)_3$, in analytical procedures. The base is amphoteric, reacting with excess alkali to form the

meta-aluminate ion. Treatment of a soluble aluminum salt with **ammonium benzoate** solution precipitates the hydroxide quantitatively in filterable form through hydrolysis of the reagent. Ammonium hydroxide produces a gelatinous precipitate of **aluminum hydroxide,** which is insoluble in the presence of ammonium salts.

Aluminon and **alizarin S Blue** form colored "lakes" with aluminum hydroxide, which is precipitated by ammonia. When the solid hydroxide is strongly heated with cobalt nitrate solution, $Co(NO_3)_2$, blue **cobalt aluminate,** $CoAl_2O_4$, Thénard's Blue, is produced.

PRELIMINARY EXPERIMENTS

1. Add NH_4OH to a test solution of Al^{+++}. Repeat the procedure, adding some solid NH_4Cl to the solution before precipitation.
2. To the test solution, add NaOH slowly until an excess has been added. Neutralize the alkaline solution with dilute HCl. Add a few more drops of acid.
3. Dilute 1 ml. of Al^{+++} test solution with an equal volume of water. Add dilute NH_4OH carefully until a very slight precipitate forms. Neutralize with dilute $HC_2H_3O_2$, add a small amount of solid NH_4Cl, and pour the solution with stirring into 1 ml. of ammonium benzoate solution. Heat on a steam bath for 4 to 5 min., filter, and wash the precipitate.
4. Place a few shreds of moist asbestos fiber in the loop of a platinum wire, dip it into some of the $Al(OH)_3$ prepared previously, and heat to dryness in the flame. Touch the loop to some dilute $Co(NO_3)_2$ solution, and heat strongly in the flame.
5. Dissolve a portion of the $Al(OH)_3$ in dilute HCl, add a few drops of ammonium acetate solution and some aluminon reagent. Make the solution alkaline with NH_4OH.
6. Repeat the foregoing procedure, using alizarin S Blue in place of the aluminon.

IRON, FE

Iron, one of the most widely used of all metals, has been known since prehistoric times. It is used primarily in the manufacture of a large number of steels and alloys. Iron falls in Group 8 of the periodic table, along with cobalt and nickel. Since iron is well above hydrogen in the electromotive series, it dissolves in both hydrochloric acid and sulfuric acid with the evolution of hydrogen. The action of nitric acid on the metal depends upon the concentration of the acid. Dilute nitric acid is reduced to ammonium ion, NH_4^+, without the evolution of any gas, and the metal is oxidized to the **ferrous** state.

With more concentrated acid, the gas NO is produced, and the iron is converted to the **trivalent** form. Concentrated nitric acid, in the cold, makes iron "passive."

In its compounds, iron exists chiefly in the di- and trivalent states. When iron is anodic, or rusting, it is believed that it exists in **tetra-** and **pentavalent** forms, but these compounds have no analytical importance and will not be considered. The trivalent form of the ion is the more stable, ferrous ion being easily oxidized in air to the ferric state. **Ferrous compounds** are pale green in solution; **ferric salts** are yellow. The **hydroxides** are not amphoteric.

Alkalis and ammonium hydroxide precipitate white to green **ferrous hydroxide,** $Fe(OH)_2$, from ferrous solutions. The precipitate is oxidized in air to brown **ferric hydroxide,** $Fe(OH)_3$; the latter may be obtained directly from ferric salts by the action of the same reagents. In the presence of ammonium salts, ferrous hydroxide is not precipitated by the action of ammonium hydroxide.

Hydrogen sulfide does not precipitate an **iron sulfide** in acid solution. In ammoniacal solution, black **ferrous sulfide,** FeS, and **ferric sulfide,** Fe_2S_3, are precipitated from the corresponding ions. Both sulfides are readily soluble in hydrochloric acid, with the evolution of hydrogen sulfide and the formation of **ferrous chloride,** $FeCl_2$. **Ammonium benzoate,** in neutral solution, precipitates the **hydroxides** of the cations through hydrolysis of the reagent.

With alkali cyanides, ferrous ion forms yellow **ferrous cyanide,** $Fe(CN)_2$, which reacts with an excess of reagent to form the soluble complex yellow **ferrocyanide (hexacyanoferrite)** ion, $[Fe(CN)_6]^{\equiv}$. This complex gives a white precipitate of **ferrous ferrocyanide,** $Fe_2[Fe(CN)_6]$, with ferrous ion; with ferric ion, it forms a deep blue precipitate, $Fe_4[Fe(CN)_6]_3$, which is called **Prussian Blue.** This reaction furnishes an extremely sensitive test for the trivalent cation. The compound itself is used as a paint pigment.

Ferric ion also forms a soluble complex with an excess of cyanide ion, the orange **ferricyanide (hexacyanoferrate)** ion, $[Fe(CN)_6]^{=}$. With **ferrous** ion, this complex forms an insoluble blue compound, **Turnbull's Blue,** $Fe_3[Fe(CN)_6]_2$; with ferric ions it forms brown $Fe[Fe(CN)_6]$. The **thiocyanate** ion, CNS^-, gives rise to an intensely red-colored solution with ferric ion; this is due to the formation of $[FeCNS]^{++}$ but the CNS^- gives no reaction with ferrous ion. This is also a sensitive test for the ferric ion and permits its detection in the presence of ferrous ion.

Alkali acetates, in an acetic acid solution of the trivalent cation, form red, un-ionized **ferric acetate,** $Fe(C_2H_3O_2)_3$. Boiling the solution

precipitates red **basic ferric acetate.** Phosphates precipitate yellowish-white **ferric phosphate,** $FePO_4$, which is insoluble in acetic acid. If phosphates are present in a solution to be analyzed, they must be removed before testing for iron (see Systematic Analysis, p. 262).

PRELIMINARY EXPERIMENTS

1. Add NH_4OH to portions of Fe^{++} and Fe^{+++} test solutions. Filter and expose a portion of $Fe(OH)_2$ to the air for several minutes.
2. Treat some Fe^{++} test solution with dilute NaOH. To the suspension add a few particles of solid Na_2O_2.
3. Make separate portions of the two test solutions ammoniacal with NH_4OH, and add some solid NH_4Cl. Saturate both solutions with H_2S. Observe the behavior of the precipitate from the ferrous salt on exposure to air. Treat separate portions of the precipitates with dilute (1:9) HCl.
4. Treat a portion of Fe^{+++} solution with some potassium ferrocyanide solution. Repeat the test with Fe^{++}. Add $K_3Fe(CN)_6$ to each of the iron test solutions.
5. Add a few drops of KCNS or NH_4CNS to a small volume of Fe^{+++} solution.
6. Carry out the reaction with ammonium benzoate, as given under Aluminum.
7. Add some $NH_4C_2H_3O_2$ solution to an acetic acid solution of ferric salt. Heat the solution to boiling.

Chromium, Cr

Chromium is placed in Group 6 of the periodic table. It is a silvery, brittle metal, soluble in acids with the evolution of hydrogen and soluble in excess alkali with the formation of the **chromite** anion CrO_2^-. In nitric acid, chromium is insoluble, becoming "passive" like aluminum and iron. Large amounts of chromium are used in the manufacture of stainless steels and in electroplating.

In its compounds, chromium usually exhibits valences of 2, 3, and 6. The divalent **chromous** compounds are very unstable, being easily oxidized in air to the more stable **chromic** ion, Cr^{+++}. Chromous compounds are, therefore, not considered in analytical procedures. **Chromic** ion may also be oxidized by chemical oxidizing agents to the hexavalent **chromate,** $CrO_4^=$, and **dichromate,** $Cr_2O_7^=$, anions.

Alkalis, ammonium hydroxide, ammonium sulfide, and ammonium carbonate precipitate gray-green to blue **chromic hydroxide,** $Cr(OH)_3$, from chromic ion solutions. **Chromic sulfide** does not exist in aqueous solution. Ammonium benzoate quantitatively precipitates the **hydrox-**

ide from neutral solutions through hydrolysis of the reagent, as mentioned previously. Chromic hydroxide is soluble in acids, with the formation of chromic salts. Since it is amphoteric, it also reacts with alkalis to form the soluble **chromite** ion, CrO_2^-. **Chromic phosphate** is greenish in color and is soluble in acetic and mineral acids.

Alkaline solutions of chromite ion and chromic hydroxide are readily oxidized to **chromate** ion with sodium peroxide, sodium hypochlorite, bromine, or chlorine. Chromic compounds are also oxidized to chromates when fused with sodium carbonate and sodium peroxide. In acid solution, **chromate** ion is converted to **dichromate** ion without any valence change:

$$Cr_2O_7^{=} + H_2O \leftrightarrows 2HCrO_4^-$$
$$H_2O + HCrO_4^- \leftrightarrows H_3O^+ + CrO_4^{=}$$

Dichromates may be obtained by strong oxidation of chromic ion in acid medium.

Barium, lead, and **silver chromates** are distinctly colored. The lead salt, known as chrome yellow, is a valuable pigment in the paint industry.

With cold sulfuric acid and hydrogen peroxide, the chromate ion gives a deep blue coloration of so-called **perchromic acid,** CrO_5, which is readily soluble in ether. This compound is unstable, but the color persists longer in the ether layer than in aqueous solution. Cold concentrated sulfuric acid forms red crystals of **chromium trioxide,** CrO_3, with dichromates and chromates. This mixture of crystals and acid is the active agent in "cleaning solution."

Ammoniacal solutions of chromate ion produce a blue-colored complex with **benzidine;** in acid solution, the same ion gives a violet color with **diphenyl carbazide.** These sensitive identification reactions also furnish an excellent example of the variation of color in coordination complexes.

PRELIMINARY EXPERIMENTS

1. Add NH_4OH to Cr^{+++} test solution until an excess has been added. Repeat the test, first adding solid NH_4Cl to the test solution. Saturate the ammoniacal solution with H_2S.

2. Precipitate $Cr(OH)_3$ with ammonium benzoate, as described previously under aluminum. Dissolve the precipitate in dilute HCl. Add NaOH slowly to a portion of the solution; then add an excess. Neutralize the alkaline solution with dilute HCl. To another portion of the alkaline solution obtained above, add Na_2O_2; heat till reaction

ceases. Acidify the solution with dilute HCl. Finally, make alkaline with NaOH.

3. Neutralize a portion of the alkaline chromate solution from the preceding experiment, and then acidify with acetic acid. Add a small amount of solid $NaC_2H_3O_2$, and then add $BaCl_2$ solution. Repeat, using concentrated $AgNO_3$ solution in place of the $BaCl_2$.

4. Neutralize a second portion of the chromate solution, acidify with acetic acid, and add a few drops of benzidine solution.

5. Make a third portion of the chromate solution acid with dilute H_2SO_4, and add an equal volume of diphenyl carbazide solution.

6. Add some H_2O_2 to a solution of chromate ion acidified with dilute H_2SO_4. Add some ether, and shake. **(CAUTION)**

NICKEL, Ni

Nickel is placed in Group 8 of the periodic table with cobalt and iron. It is a hard, silvery-white magnetic metal that may be converted to the passive state by treatment with concentrated nitric acid. In finely divided form, nickel is an excellent catalyst for the hydrogenation of fats, oils and many classes of organic compounds. The metal is also used extensively in the making of coins and alloys and in electroplating. Some of the important nickel alloys are nickel steel, Nichrome, and Monel metal.

Although **nickel** is above hydrogen in the electromotive series, it is difficultly soluble in hydrochloric acid and sulfuric acid but is readily soluble in moderately concentrated nitric acid. The nickel cation usually exhibits a valence of 2. In solution, it is pale green; the anhydrous salts, however, are yellow. Alkalis precipitate **nickelous hydroxide,** $Ni(OH)_2$, which is insoluble in excess reagent but is soluble in acids. Ammonium hydroxide precipitates, from **nickel sulfate** solution, the **green basic salt,** $Ni_2SO_4(OH)_2$, which is soluble in excess reagent with the formation of the **complex ion,** $[Ni(NH_3)_6]^{++}$. If ammonium salts are present in the ammonium hydroxide, no precipitate is obtained, the deep blue complex ion being formed immediately. Alkali carbonates precipitate apple-green **nickelous carbonate,** $NiCO_3$. The corresponding compound produced with ammonium carbonate is soluble in excess reagent with the formation of the complex **hexammino salt.**

In acid solution, the sulfide ion concentration of hydrogen sulfide is not sufficient to precipitate **nickel sulfide.** In neutral or ammoniacal solution, black **nickel sulfide,** NiS, is readily formed. The sulfide is very slowly soluble in 1:9 HCl, slowly soluble in the concentrated acid, and readily soluble in nitric acid and aqua regia.

Solutions of nickelous ion give a brilliant red crystalline precipitate with **dimethyl glyoxime** when made faintly ammoniacal. The borax bead obtained with nickel ion is reddish brown in color in the oxidizing flame.

PRELIMINARY EXPERIMENTS

1. Add dilute NH_4OH dropwise to Ni^{++} test solution, until an excess has been added. Repeat the foregoing, adding solid NH_4Cl to the test solution. Saturate the ammoniacal solution with H_2S. Filter and wash the precipitate.
2. Treat a portion of the sulfide with 1:9 HCl. Treat separate portions of the precipitate with HNO_3 and aqua regia.
3. Make a portion of the test solution ammoniacal, and place a drop on a spot plate. Treat with an equal volume of dimethyl glyoxime. Acidify with HCl; make ammoniacal again.
4. Fuse some borax in the loop of a platinum wire. Cool the bead, moisten with water, and touch it to the surface of a dilute Ni^{++} solution. Heat strongly in the oxidizing flame.

Cobalt, Co

Cobalt, a steel-gray magnetic metal, was first isolated in the early nineteenth century. It is placed in Group 8 of the periodic table and is just above nickel in the electromotive series. Cobalt forms many alloys, among them the extremely hard stellite and carboloy. It is used to impart a blue color to glass and enamel and also as an oxidation accelerator for drying oils. The metal is readily soluble in dilute nitric acid and in hot, dilute hydrochloric and sulfuric acids. With concentrated solutions of nitric acid, cobalt becomes passive.

The **cobalt cation** generally exhibits a valence of 2. Simple trivalent cobaltic salts are unknown and exist only in complex compounds like the **cobaltinitrites (nitritocobaltates), cobalticyanides (cyanocobaltates),** and **complex ammines.** In contrast to the pink color of the hydrated ion, anhydrous cobaltous salts are blue. Use is made of this sharp color difference in the manufacture of simple weather indicators.

Alkalis precipitate a blue, **basic cobalt salt,** which decomposes on heating to pink **cobaltous hydroxide,** $Co(OH)_2$. This is oxidized in air to the brown **cobaltic hydroxide,** $Co(OH)_3$. Ammonium hydroxide also precipitates a **blue basic salt,** which is soluble in ammonium chloride, forming a brown solution that is gradually oxidized in air to the very stable **chlorpentamminocobaltic chloride,** $[Co(NH_3)_5Cl]Cl_2$.

Alkali carbonates precipitate a reddish colored **basic cobalt carbonate** that is soluble in ammonium carbonate and ammonium chloride.

High concentrations of sulfide ion, such as are obtained in neutral or ammoniacal solution, precipitate black **cobalt sulfide,** CoS, which is very slowly soluble in 1:9 HCl and in acetic acid. The sulfide is readily soluble in nitric acid and aqua regia with the separation of elementary sulfur.

When concentrated solutions of cobaltous ion are treated with soluble nitrites and acetic acid, the complex **cobaltinitrite (hexanitritocobaltate)** ion, $[Co(NO_2)_6]^{\equiv}$, is produced. If potassium nitrite is used in this preparation, a crystalline yellow precipitate of **potassium cobaltinitrite** is obtained. When concentrated solutions of ammonium thiocyanate, NH_4CNS, are added to cobaltous salts, a blue solution of the complex **cobaltithiocyanate (tetrathiocyanatocobaltate)** ion, $[Co(CNS)]_4^{=}$, is obtained. The complex is very soluble in amyl alcohol or a mixture of amyl alcohol and ether, which intensifies the color. The addition of acetone to the solution also intensifies the color. Ferric ion, in small amounts, interferes with this test, but the interference may be minimized by the addition of tartaric acid to the solution before testing.

A purple-red precipitate is obtained when a freshly prepared solution of **α-nitroso-β-naphthol** is added to an acetic acid solution of cobalt ion. The colored precipitate is insoluble in cold, dilute acids. The borax bead coloration in either the oxidizing or reducing flame is blue. This is an extremely sensitive and conclusive test.

PRELIMINARY EXPERIMENTS

1. Pass H_2S into an ammoniacal solution of cobalt ion, containing some ammonium chloride. Treat a portion of the precipitate with a few drops of 1:9 HCl. Add aqua regia to a second portion of the sulfide.

2. Prepare a borax bead as described previously, and touch it to a little of the cobalt sulfide. Heat strongly in the oxidizing flame.

3. Acidify a portion of a concentrated Co^{++} solution with dilute $HC_2H_3O_2$, saturate the solution with solid KCl, and then add an excess of KNO_2 solution.

4. Make a portion of the test solution acid with acetic acid. Place a drop of the solution on a spot plate, and add an equal volume of α-nitroso-β-naphthol solution.

5. Acidify 1 ml. of test solution with acetic acid; treat with an equal volume of NH_4CNS solution in acetone.

Manganese, Mn

Manganese is a grayish-white metal that is very easily oxidized in moist air. It was discovered in 1774 by the Swedish chemist Scheele. It is a transition element, falling in Group 7 of the periodic table. The metal is used in the manufacture of certain types of steel, in dry cells in the form of manganese dioxide, MnO_2, as a dryer for paints and oils, and as a coloring agent for glass and ceramics.

Manganese is a fairly active element, being in the upper part of the electromotive series, just below aluminum. It reacts with warm water, evolving hydrogen and forming a precipitate of **manganous hydroxide,** $Mn(OH)_2$. It is readily attacked by dilute mineral acids, forming manganous ions.

The element exists in a number of valence states—2, 3, 4, 6, and 7. It exhibits, also, a gradation of properties, ranging from a basic cation in Mn^{++} to the strongly acidic anion, MnO_4^-, where manganese has a valence of 7. The **divalent manganese** ion is most generally used in analytical procedures. It forms pink compounds, both in solution and in crystalline form, but is colorless when anhydrous. Alkalis precipitate white **manganous hydroxide** from manganous ion test solution; this turns brown in air due to oxidation to $MnO(OH)_2$. Manganous hydroxide is insoluble in excess reagent but is soluble in ammonium salts before oxidation. Ammonium hydroxide precipitates the base incompletely, and not at all in the presence of ammonium salts.

Sulfide ion precipitates pink **manganous sulfide,** MnS, from ammoniacal solution. The sulfide is soluble in hydrochloric acid. By the action of hydrogen sulfide on a hot ammoniacal solution of manganous ion, green MnS may be precipitated. The same compound may be obtained by the reduction of **manganate,** $MnO_4^{=}$, and **permanganate** ions in alkaline solution, in the presence of sulfide ion. All the higher valence forms are reduced to manganous ion by sulfide ion. Sulfites reduce manganate and permanganate ion to **manganese dioxide,** MnO_2, in neutral solution and to **manganous** ion in acid solution.

Oxidizing agents, like sodium peroxide and sodium hypobromite, convert manganous ion to manganese dioxide. Stronger oxidizing agents, like **lead dioxide,** PbO_2, in acid solution or **ammonium persulfate** in the presence of silver nitrate or **sodium bismuthate,** $NaBiO_3$, oxidize manganous and manganic ions to the violet-colored **permanganate** ion, MnO_4^-. Halogen acids function as reducing agents when treated with the higher oxidized forms, MnO_2, $MnO_4^{=}$, and MnO_4^-, the free halogen being produced. Oxidative fusion of manganous

hydroxide with sodium carbonate produces a green bead of **sodium manganate.**

PRELIMINARY EXPERIMENTS

1. Treat Mn^{++} test solution with NH_4OH. Add solid NH_4Cl to the suspension. Add a mixture of NH_4OH and NH_4Cl to another portion of the test solution.

2. Saturate an ammoniacal solution of Mn^{++} with H_2S. Boil the suspended solid. Filter and ascertain the solubility of the sulfide in 1:9 HCl.

3. Add NH_4OH to a portion of the test solution. Treat the precipitate with a small amount of solid Na_2O_2. Acidify a portion of the test solution with dilute HNO_3, add a crystal of $KClO_3$, and heat to boiling. Cool, and repeat the treatment. Save the precipitate for experiments 4 and 5.

4. To a portion of the washed precipitate from experiment 3, add dilute HNO_3 and a few drops of H_2O_2. Boil to expel excess peroxide, cool, and add a few crystals of $NaBiO_3$. Shake, and allow the solid to settle.

5. Dissolve another portion of the washed precipitate from experiment 3 in dilute HNO_3, add 1 drop of $AgNO_3$ solution and a few crystals of ammonium persulfate, and warm.

6. Fuse a small amount of Na_2CO_3 in the loop of a platinum wire, and dip it into some $Mn(OH)_2$. Heat in the flame, touch the bead to some powdered $KClO_3$, and heat again.

ZINC, Zn

Zinc is a bluish-white low-melting metal that is placed in Group 2 of the periodic table. It finds wide use in commerce as a protective coating for iron (galvanizing), as a constituent of paint pigments, as a component of alloys, notably brass, in dry cells and in pharmaceutical preparations.

The metal is above hydrogen in the electromotive series and dissolves in hydrochloric and sulfuric acids. It is, however, a strong reducing agent and gives nitrogen dioxide, nitric oxide, and ammonia with varying concentrations of nitric acid. Like aluminum, it is soluble in alkalis with the evolution of hydrogen and the formation of the amphoteric **zincate ion,** $ZnO_2^{=}$.

The zinc cation exists only in a valence of 2. Alkali hydroxides precipitate white **zinc hydroxide,** $Zn(OH)_2$, which is soluble in excess reagent with the formation of the **zincate ion,** $ZnO_2^{=}$. In the absence of ammonium salts, ammonium hydroxide precipitates **zinc hydroxide,**

which is soluble in excess reagent with the formation of the colorless **hexammino zinc** ion, $[Zn(NH_3)_6]^{++}$. Ammonium sulfide precipitates white **zinc sulfide,** ZnS, from alkaline, neutral, or faintly acid solutions of zinc ion. Hydrogen sulfide will precipitate **zinc sulfide** from neutral solution or from a strongly buffered acetic acid solution. When zinc ion is added to a mixture of **diphenylamine acetate** and **potassium ferricyanide,** it catalyzes the oxidation of the amine; dark-colored products result. **Pyridine** and **ammonium thiocyanate** produce a heavy white precipitate with Zn ion; strong heating of a mixture of the ion with potassium cobalticyanide and potassium chlorate or with dilute cobalt nitrate solutions produces a green residue (Rinman's Green).

PRELIMINARY EXPERIMENTS

1. Pass H_2S into an ammoniacal solution of Zn^{++} test solution. Neutralize a portion of the test solution with NH_4OH; then make just acid with acetic acid. Add some solid $NH_4C_2H_3O_2$, and saturate the solution with H_2S.

2. Add NH_4OH cautiously to the test solution until an excess has been added. Repeat, first adding an equal volume of NH_4Cl solution to the Zn^{++} test solution.

3. Carefully add NaOH to the test solution until an excess has been added. Neutralize the solution with dilute HCl.

4. Make a portion of the test solution faintly acid with acetic acid. Add 1 drop of diphenylamine acetate solution (1 g. of the amine in 100 ml. of glacial acetic acid) and 1 ml. of 5% $K_3Fe(CN)_6$ solution. A greenish black turbidity is indicative of the presence of zinc.

5. To a portion of the *neutral* test solution, add 1 drop of pyridine and several drops of NH_4CNS solution.

6. Place a drop of the neutral test solution on a piece of filter paper that has been treated with $KClO_3$ and $K_3Co(CN)_6$ reagent. Roll the paper into a small ball, and heat strongly in the loop of a platinum wire or in a crucible.

(*Alternate procedure*) Place a few shreds of moist asbestos fiber in the loop of a platinum wire, dip it into some $Zn(OH)_2$, and heat to dryness in the flame. Touch to some dilute $Co(NO_3)_2$ solution, and heat strongly in the flame.

ANALYSIS OF GROUP III CATIONS

Outline of Separations

The cations of Group III are precipitated from an ammoniacal solution containing ammonium chloride and ammonium sulfide, the

latter resulting from the neutralization of the base by hydrogen sulfide. Co^{++}, Ni^{++}, Fe^{++}, Mn^{++}, and Zn^{++} are precipitated as sulfides; Al^{+++} and Cr^{+++} are obtained as the hydroxides.

The entire precipitate is redissolved in aqua regia and separated into two subgroups. The *A* subgroup, Al, Fe, and Cr, is precipitated as hydroxide in easily filterable form by the use of ammonium benzoate in neutral solution, leaving subgroup *B* in the filtrate. Sufficient hydroxyl ion for this precipitation and separation is furnished by hydrolysis of the ammonium benzoate.

The hydroxides of subgroup *A* are redissolved, and on boiling with sodium peroxide and sodium hydroxide, Fe is reprecipitated as the hydroxide, leaving Al in the form of the soluble aluminate, while Cr is oxidized to $CrO_4^{=}$. Aluminum is then separated by precipitation in a weakly alkaline medium.

Subgroup *B* ions are reprecipitated as the sulfides; NiS and CoS are separated from MnS and ZnS by their insolubility in 1:9 HCl. Manganese is precipitated from the solution as MnO_2 and thus separated from zinc.

Analytical Procedure

The unknown solution may be the H_2S-free slightly acid filtrate from the Group II separation, or it may be a mixture containing the cations of this group only.

1. Make the volume of solution up to 4 ml. with distilled water, add approximately 0.25 g. of solid NH_4Cl, and stir until it is completely dissolved. Add NH_4OH until the solution is slightly alkaline to litmus; warm and saturate with H_2S. When precipitation is complete, filter and wash the precipitate carefully with distilled water. If the filtrate is to be used for further analysis, boil it with a few drops of glacial acetic acid to expel H_2S, filter if necessary, and reserve for Groups IV and V.

2. Redissolve the precipitate in the least volume of aqua regia required, evaporate almost to dryness, dilute with 1 ml. of water, and filter if necessary. Add NH_4OH to the filtrate until a very slight precipitate forms. Clear the solution with acetic acid, add a few crystals of NH_4Cl and 1 ml. of ammonium benzoate solution. Dilute to 10 ml. with distilled water, and heat on a steam bath for 4 to 5 min. Cool, filter, and wash the precipitate several times. Combine the filtrate and washings, and reserve for Group III*B* analysis (step 8).

subgroup *A*

In addition to the hydroxides of Al, Fe, and Cr, the precipitate also contains a small amount of benzoic acid.

3. Boil the precipitate with about 0.5 ml. of dilute HCl. Evaporate to a small volume, add 1 ml. of water, and filter. Discard the precipitate of benzoic acid.

4. Make the solution slightly alkaline with dilute NaOH, and add a small amount of Na_2O_2. Boil gently for about 2 min., cautiously adding small amounts of Na_2O_2 from time to time, with stirring, until an excess has been added. Cool the solution, add several drops of water, filter, and wash the precipitate with cold water. Combine the filtrate and washings and save for the Al and Cr tests in step 6.

NOTE: Care should be taken not to add the peroxide too rapidly because of the violent reaction of Na_2O_2 and water. Sodium peroxide should be transferred in small quantities from the container to a watch glass and *never onto filter paper.*

5. Add just enough dilute HCl to the precipitate to dissolve it completely, and dilute the solution with 3 to 4 drops of water. Place 1 drop of the solution on a piece of filter paper, and add an equal volume of $K_4Fe(CN)_6$ solution.

Deep blue precipitate of Prussian Blue indicates **ferric ion.**

Place 2 drops of the solution on a spot plate, and add 1 drop of KCNS solution.

Intense red coloration of $(FeCNS)^{++}$ proves **ferric ion.**

6. Make the filtrate from step 4 slightly acid with dilute HCl.

NOTE: The acid should be added cautiously while the solution is being cooled under running water to prevent reduction of CrO_4^{--} to Cr^{+++}.

Add a small amount of solid NH_4Cl; then make alkaline with NH_4OH, and heat to boiling.

NOTE: The NH_4OH should be added to the solution until, after blowing away the vapors of NH_3, the solution has a distinctly ammoniacal odor.

Gelatinous precipitate indicates **aluminum.**

Filter, and save the filtrate for step 7. Dissolve the precipitate in dilute HCl. Place a few drops of the solution in a test tube, add 1 drop of alizarin S Blue, and make slightly ammoniacal.

Blue "lake" indicates presence of **aluminum.**

Place the remainder of the acid solution in a test tube, add 2 drops of aluminon reagent, and make the solution slightly ammoniacal.

Red "lake" confirms the presence of **aluminum.**

NOTE: If chromium is present, the filtrate from the aluminum separation will be yellow.

7. Evaporate the solution from step 6 to a small volume, and make it slightly acid with dilute H_2SO_4. Place 1 drop of the solution on a spot plate, and add an equal volume of diphenyl carbazide solution.

Violet-blue coloration indicates **chromium.**

Place the remainder of the solution in a test tube, and add an equal volume of ether. Add a few drops of H_2O_2, and mix thoroughly by shaking.

Blue color in upper (ether) layer proves **chromium.**

NOTE: Since ether is highly inflammable, it should be kept away from open flames. If the tube has been stoppered before shaking, care should be exercised in removing the stopper so that the volatile contents are not splashed about and into the face.

SUBGROUP *B*

The filtrate from step 2 contains the cations Ni^{++}, Co^{++}, Mn^{++}, and Zn^{++} and some ammonium benzoate.

8. Add sufficient HCl to render the solution distinctly acid, and filter off the precipitated benzoic acid. Make the filtrate slightly ammoniacal, add a few crystals of NH_4Cl, heat to boiling, and pass in H_2S until precipitation is complete. Filter, wash the precipitate, and discard the filtrate.

9. Place the precipitate in a crucible, add 1 ml. of 1:9 HCl, and allow the solid to digest in the cold for 8 to 10 min., stirring frequently. Filter, and reserve the filtrate for step 12.

NOTE: Under these conditions, MnS and ZnS are dissolved completely, leaving a black residue of NiS and CoS. If the digestion is permitted to proceed too long, small amounts of nickel and cobalt sulfides will be dissolved.

10. Dissolve the black precipitate in aqua regia, evaporate almost to dryness, take up the residue with 1 ml. of water, filter, and discard the precipitate. Place a drop of the solution on a spot plate, add dilute NH_4OH until the solution is basic, and then add a drop of dimethyl glyoxime solution.

Red precipitate proves presence of **nickel.**

11. Place a few drops of the solution from step 10 in a test tube, and make distinctly acid with acetic acid. Add 2 drops of a freshly prepared solution of α-nitroso-β-naphthol.

Intense red precipitate proves **cobalt.**

To the remainder of the preceding solution add a solution of NH_4CNS in acetone.

Blue color proves **cobalt.**

12. Make the filtrate from step 9 alkaline with NaOH, add a few granules of Na_2O_2, and heat gently for about 1 min. Repeat the treatment several times. Dilute the solution with a few drops of water, filter, and wash the precipitate with cold water. Combine the filtrates, and reserve for step 14.

NOTE: The precipitate is hydrated MnO_2; the solution contains $ZnO_2^{=}$ ion.

13. Wash part of the precipitate thoroughly with water and then dissolve it in hot dilute HNO_3. Add a few drops of H_2O_2. Boil to *decompose* excess peroxide, cool, and add a little solid $NaBiO_3$. Shake and permit the solid to settle.

Purple coloration of MnO_4^- proves **manganese.**

14. Make a portion of the zinc filtrate from Step 12 just acid with acetic acid, add some solid $NH_4C_2H_3O_2$ and saturate with H_2S.

White precipitate of ZnS indicates **zinc.**

Make another portion of the alkaline solution faintly acid with acetic acid. Add 1 drop of diphenylamine acetate solution and 1 ml. of 5% $K_3Fe(CN)_6$.

Greenish-black turbidity proves the presence of **zinc.**

ANALYTICAL TABLE V

ANALYSIS OF GROUP III

The filtrate from Analytical Table II (separation of Group II) may contain Ni^{++}, Co^{++}, Fe^{++}, Fe^{+++}, Mn^{++}, Al^{+++}, Cr^{+++}, and Zn^{++}, as well as the cations of Groups IV and V. Make the filtrate ammoniacal, add solid NH_4Cl, and saturate with H_2S. Filter, boil the filtrate with glacial $HC_2H_3O_2$, and reserve for the Groups IV and V analysis [Analytical Tables VIII and IX (**1**)]. Dissolve the precipitate in aqua regia, evaporate almost to dryness, take up in H_2O, and filter if necessary. Add NH_4OH until a slight precipitate forms, clear with $HC_2H_3O_2$, add solid NH_4Cl and ammonium benzoate solution. Dilute with H_2O to 10 ml., heat, cool, and filter (**2**).

Precipitate: $Al(OH)_3$ (white), $Fe(OH)_3$ (red-brown), $Cr(OH)_3$ (gray-green). (Group III*A*.) Proceed as in Analytical Table VI.	**Filtrate:** Ni^{++}, Co^{++}, Mn^{++}, Zn^{++}. (Group III*B*.) Proceed as in Analytical Table VII.

ANALYTICAL TABLE VI

ANALYSIS OF GROUP III*A*

Boil the precipitate from Analytical Table V with dilute HCl, treat with H_2O, filter, and discard the precipitate of benzoic acid (**3**). Make the solution alkaline with NaOH, add excess Na_2O_2 in small portions, and boil for several minutes. Cool, dilute with H_2O, and filter. Wash the precipitate, and combine the filtrate and washings (**4**).

Precipitate: $Fe(OH)_3$. Dissolve in dilute HCl, and test portion with $K_4Fe(CN)_6$ solution. Confirm with KCNS solution (**5**).

Filtrate: AlO_2^-, $CrO_4^=$ (yellow solution if $CrO_4^=$ present). Acidify with dilute HCl, add solid NH_4Cl, make ammoniacal, boil, and filter (**6**).

- **Precipitate:** $Al(OH)_3$. Dissolve in dilute HCl, and test portion with alizarin S in ammoniacal solution. Confirm with aluminon reagent (**6**).
- **Filtrate:** $CrO_4^=$. Evaporate and acidify with dilute H_2SO_4. Test with H_2O_2 and ether, and confirm with diphenyl carbazide solution (**7**).

ANALYTICAL TABLE VII

ANALYSIS OF GROUP III*B*

Acidify the filtrate from Analytical Table V with HCl, and discard the precipitate of benzoic acid. Make the filtrate ammoniacal, add solid NH_4Cl, boil, and saturate with H_2S: NiS (black), CoS (black), MnS (pink), ZnS (white). Filter, wash the precipitate, and discard the filtrate (**8**). Treat the precipitate with 1:9 HCl for several minutes, and filter (**9**).

Precipitate: NiS, CoS. Dissolve in aqua regia, evaporate almost to dryness, add H_2O, filter, and discard the precipitate. Test one portion for Ni^{++} with dimethyl glyoxime (**10**). Test for Co^{++} with α-nitroso-β-naphthol, and confirm with NH_4CNS-acetone test (**11**).

Filtrate: Mn^{++}, Zn^{++}. Make alkaline with NaOH, add Na_2O_2, and heat. Cool, and repeat treatment several times. Dilute with H_2O, filter, wash precipitate, and combine washings and filtrate (**12**).

- **Precipitate:** MnO_2 (hydrated, brown). Dissolve portion of precipitate in hot HNO_3-H_2O_2 mixture, boil, and test with $NaBiO_3$ (**13**).
- **Filtrate:** $ZnO_2^=$. Make a portion acid with $HC_2H_3O_2$, add solid $NH_4C_2H_3O_2$, and saturate with H_2S. Confirm with the diphenylamine acetate and $K_3Fe(CN)_6$ test (**14**).

GROUP IV CATIONS

CALCIUM, Ca

Calcium is a silvery-white metal that tarnishes rapidly in air. Since it falls in Group 2 of the periodic table, its hydroxide is a strong base, although it is not very soluble in water. Calcium is divalent in all its compounds.

Compounds of calcium are widely distributed over the earth's crust. It occurs chiefly as the **carbonate** (marble, calcite, chalk, limestone) and as the **sulfate** (gypsum). It finds application in industry as plaster, [calcium hydroxide, $Ca(OH)_2$], plaster of Paris (calcium sulfate hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$), and in building materials.

Ammonium carbonate and ammonium hydroxide precipitate the **carbonate** almost completely from calcium ion solutions. Calcium carbonate is insoluble in water, but it is appreciably soluble in the ammonium salts of strong acids (ammonium chloride, ammonium sulfate). Chromate ion precipitates yellow **calcium chromate,** $CaCrO_4$, from concentrated solutions of calcium ion. The precipitate is soluble in water and acetic acid. White **calcium oxalate,** CaC_2O_4, is precipitated by the action of oxalate ion on soluble calcium salts. It is insoluble in water and acetic acid but is readily soluble in mineral acids. **Calcium sulfate** is only slightly soluble in water.

Calcium compounds color the flame brick-red. With the **hand spectroscope,** the chief lines observed are a yellowish green to one side of the sodium line and an orange-yellow double line on the other side.

PRELIMINARY EXPERIMENTS

1. Add ammonium carbonate solution to a portion of Ca^{++} test solution. Treat the precipitate with acetic acid.

2. To the test solution, add some K_2CrO_4 solution. Treat some of the solution with two or three times its volume of ethyl alcohol, noting the volume added. Add acetic acid to the precipitate.

3. Add dilute H_2SO_4 to the test solution.

4. Treat a portion of the test solution with ammonium oxalate solution. Test the solubility of the precipitate in acetic and mineral acids.

5. Perform a flame test on a calcium salt.[1] Observe the flame both with the naked eye and with the hand spectroscope.

STRONTIUM, Sr

Strontium is very similar to calcium in many ways. The pure metal is generally described as silver-white, although some observers claim that it is brass-yellow. It is believed that this tint is due to impurities. Strontium falls in the same group of the periodic table as calcium.

Strontium ion, divalent in all its compounds, is similar to calcium in its reactions with **ammonium carbonate** and **ammonium oxalate.** The **chromate,** $SrCrO_4$, is less soluble than calcium chromate but

[1] See Flame Tests, Blowpipe Analysis, p. 220.

much more soluble than barium chromate. The same relationship exists among the **sulfates** of the three cations of this analytical group.

Strontium compounds color the flame crimson. This fact is used in the manufacture of fireworks and flares containing strontium salts. Viewed in the **hand spectroscope,** the spectrum of strontium shows a number of lines in the red and orange-yellow portions and one line in the **blue** region.

PRELIMINARY EXPERIMENTS

1. Treat a portion of Sr^{++} test solution with $(NH_4)_2CO_3$ solution. Add acetic acid to the precipitate.
2. Add K_2CrO_4 solution to the test solution. Treat some of the solution with ethyl alcohol, noting the comparative volume added. Treat the precipitate with acetic acid.
3. Add dilute H_2SO_4 to a portion of Sr^{++} test solution.
4. To a portion of test solution, add $(NH_4)_2C_2O_4$ solution. Test the solubility of the precipitate in acetic and mineral acids.
5. Perform a flame test on a strontium salt. Observe the colored flame with the naked eye and with a hand spectroscope.

Barium, Ba

Barium is usually described as a silver-white metal and is placed in Group 2 of the periodic table. It resembles both calcium and strontium in its chemical properties. Soluble barium salts are extremely poisonous. **Barium sulfide,** BaS, is soluble in water and is often used as a depilatory.

Barium carbonate, $BaCO_3$, exhibits chemical properties similar to those of calcium carbonate. Yellow **barium chromate,** $BaCrO_4$, is precipitated from neutral solution by alkali chromates. It is insoluble in acetic acid. Oxalate ion precipitates white **barium oxalate,** BaC_2O_4, which is insoluble in water, although it is more soluble than the corresponding calcium and strontium salts. It is readily soluble in hot dilute acetic acid. Sulfate ion precipitates white **barium sulfate,** $BaSO_4$, which is very insoluble in water and hot concentrated mineral acids.

The barium flame is yellowish green. In the **hand spectroscope,** there can be seen numerous deep green and some weak green lines in the spectrum.

PRELIMINARY EXPERIMENTS

1. Add $(NH_4)_2CO_3$ to Ba^{++} test solution. Treat the precipitate with acetic acid.

2. Treat a neutral solution of Ba^{++} with K_2CrO_4 solution. Test the solubility of the precipitate in acetic acid.

3. To the test solution, add $(NH_4)_2C_2O_4$ solution.

4. Treat a portion of the test solution with dilute H_2SO_4. Test the solubility of the precipitate in hot water and mineral acids.

5. Perform a flame test on Ba^{++} test solution. Observe with the naked eye and with the hand spectroscope.

6. (*Optional*) Test lithopone pigment for barium as follows: Mix powdered charcoal with the lithopone, and hold in the flame in the loop of a platinum wire. Moisten with dilute HCl, and hold in the flame again.

ANALYSIS OF GROUP IV CATIONS

Outline of Separations

The metals of Groups IV and V are converted to the chlorides, and any excess ammonium salts present are removed. The cations of this group are then precipitated individually from solution, no group reagent being employed.

Barium ion is precipitated as the chromate, strontium as the sulfate, and calcium as the oxalate. The remaining solution is reserved for the analysis of Group V.

Analytical Procedure

1. Evaporate the filtrate from previous group separations to a small volume, filter, and discard any precipitate. Add concentrated HCl (1 ml./ml. of solution), and again evaporate to a very small volume but not to dryness. Again add the same volume of concentrated HCl, and evaporate just to dryness. **DO NOT IGNITE.** Add about 1 ml. of distilled water, and again evaporate cautiously just to dryness. Dissolve the residue in about 1 ml. of $0.2N$ HCl. (All the material should dissolve.)

2. Heat the solution to boiling, and add an $0.5N$ solution of $(NH_4)_2CrO_4$, drop by drop, until precipitation is complete.

Yellow precipitate indicates **barium.**

Note: The solution should be kept warm and the $(NH_4)_2CrO_4$ added dropwise until further addition produces no turbidity in the clear supernatant liquid. The coloration of the solution at this point should be intensely yellow.

Filter, and save the filtrate for step 3. Confirm the presence of barium in the precipitate by a flame test.

Yellowish-green flame confirms **barium.**

3. Heat the filtrate from step 2 to 70 to 80°C., and add a solution of $0.5N$ $(NH_4)_2SO_4$ dropwise until no further precipitation occurs. Filter, and reserve the filtrate for step 4.

White precipitate indicates **strontium.**

Confirm the presence of strontium with a flame test.

Crimson flame confirms **strontium.**

4. Heat the filtrate from step 3 to boiling, and add an $0.5N$ solution of $(NH_4)_2C_2O_4$ until no further precipitation occurs. Filter, and reserve the solution for the analysis of Group V.

White precipitate indicates **calcium.**

Perform a flame test as confirmation of the presence of calcium in the precipitate.

Brick-red flame proves **calcium.**

ANALYTICAL TABLE VIII

Analysis of Group IV

The filtrate from Analytical Table V (separation of Group III) may contain Ba^{++}, Sr^{++}, and Ca^{++}, as well as the Group V cations. Evaporate, filter and discard the precipitate. Treat with concd. HCl, and evaporate to a small volume. Repeat the treatment, and evaporate to dryness. **DO NOT IGNITE.** Dilute with H_2O, and again evaporate to dryness. Take up the residue in 1 ml. of $0.2N$ HCl (**1**). Heat the solution to boiling, and treat with $0.5N$ $(NH_4)_2CrO_4$ solution (**2**). Filter.

<table>
<tr><td rowspan="2">Precipitate: $BaCrO_4$ (yellow). Confirm Ba^{++} with flame test (2).</td><td colspan="2">Filtrate: Sr^{++}, Ca^{++}. Heat, and treat with $0.5N$ $(NH_4)_2SO_4$ solution. Filter (3).</td></tr>
<tr><td>Precipitate: $SrSO_4$ (white). Confirm Sr^{++} with flame test (3).</td><td>Filtrate: Ca^{++}. Boil, and treat with $0.5N$ $(NH_4)_2C_2O_4$ solution. Filter, and reserve filtrate for Group V analysis. Confirm Ca^{++} in precipitate with flame test (4).</td></tr>
</table>

GROUP V CATIONS

Magnesium, Mg

Magnesium is a silvery white metal that is so light that it is now replacing aluminum in the manufacture of lightweight alloys. Since it burns with a brilliant white flame, it is used in flashlight powders in

photography. Magnesium falls in Group 2 of the periodic table and is therefore an alkaline earth element.

Magnesium hydroxide, $Mg(OH)_2$, is a strong base, although it is very insoluble in water. It is, however, soluble in ammonium salts. The **carbonate,** $MgCO_3$, behaves similarly in its solubility. Almost all magnesium compounds are colorless. There are known, however, the so-called **lakes,** which are highly colored. Notable among these is the "lake" obtained with magnesium hydroxide and ***p*-nitrobenzene-azo-resorcinol,** which is colored blue. With ammonium and phosphate ions, magnesium precipitates as white **magnesium ammonium phosphate,** $MgNH_4PO_4$, which is quite insoluble in water.

PRELIMINARY EXPERIMENTS

1. Cautiously add NH_4OH to a portion of Mg^{++} test solution. To another portion of the test solution, add one-half its volume of a saturated solution of NH_4Cl, and then add NH_4OH as before.
2. To a few drops of the neutral or slightly acid test solution, add a drop of *p*-nitrobenzene-azo-resorcinol solution. Make the solution strongly alkaline with NaOH. Run a blank test simultaneously.
3. Acidify a portion of the test solution with dilute HCl, and heat to boiling. Add Na_2HPO_4 solution to the hot solution. Add dilute NH_4OH equal to one-third the volume of solution, and allow to cool.
4. (*Optional*) Test some "milk of magnesia" for magnesium ion by any one of the preceding methods.

Potassium, K

Potassium belongs to the family of alkali metals comprising Group 1 of the periodic table. Freshly cut surfaces of the metal are silvery white. Potassium reacts violently with water, with the evolution of hydrogen and the formation of the strong, soluble **hydroxide,** KOH. The metal itself is not used commercially to any great extent, but the chloride and sulfate are used as fertilizer ingredients.

Most of the potassium salts are soluble. With perchlorate ion, white **potassium perchlorate,** $KClO_4$, is precipitated. Picric acid yields yellow **potassium picrate;** a mixture of silver nitrate and sodium cobaltinitrite precipitates yellow **dipotassium silver hexanitritocobaltate,** $K_2AgCo(NO_2)_6$. Bismuth nitrate and sodium thiosulfate yield a yellow precipitate of $K_3Bi(S_2O_3)_3$, **tertiary potassium trithiosulfatobismuthite.** A yellow precipitate of **potassium chloroplatinate,** K_2PtCl_6, is obtained with the chloroplatinate ion. Other insoluble salts are also known.

Potassium salts give a characteristic violet flame test which, when viewed through a cobalt glass, is red-violet.

PRELIMINARY EXPERIMENTS

1. Add perchloric acid, $HClO_4$, to about 0.5 ml. of K^+ test solution. (**CAUTION:** Do not heat.)

2. To another portion of the test solution, add a saturated solution of picric acid.

3. To 1 drop of a neutral or slightly acid (acetic acid) solution of K^+, add a drop of an 0.05% solution of $AgNO_3$ and a small amount of solid $Na_3Co(NO_2)_6$.

4. Add Carnot's reagent to the test solution.

Carnot's reagent: Mix 1 drop of 0.5*N* $Bi(NO_3)_3$ with 2 to 3 drops of 0.5*N* $Na_2S_2O_3$ and 10 to 15 ml. of absolute alcohol. Any turbidity is removed by adding a very small amount of H_2O.

5. Perform a flame test on the test solution, viewing the flame through two or three thicknesses of cobalt glass.

6. (*Optional*) Plants contain appreciable amounts of potassium salts. Test the ash of a cigarette for potassium by means of the flame test. Moisten the ash with concentrated HCl before touching the platinum wire to it.

Sodium, Na

Sodium belongs to the family of alkali metals. The freshly cut surface of the metal is silvery white, but it tarnishes very rapidly. It reacts rapidly and violently with water, liberating hydrogen and forming the soluble **hydroxide,** NaOH, which is a strong base.

Very few sodium salts are insoluble. With zinc uranyl acetate, yellow **sodium zinc uranyl acetate,** $NaZn(UO_2)_3(C_2H_3O_2)_9 \cdot 6H_2O$, is precipitated. Potassium antimonate precipitates white **sodium antimonate,** NaH_2SbO_4, formerly erroneously called the pyroantimonate.

Sodium ion, even in very slight concentrations, gives a yellow flame test. One must therefore distinguish carefully between a trace of sodium (present as impurity) and an appreciable amount.

PRELIMINARY EXPERIMENTS

1. Add some fairly concentrated Na^+ test solution to the zinc uranyl acetate reagent.

2. Perform a flame test on the test solution. Repeat the test on a solution of NH_4Cl.

3. (*Optional*) The human body excretes, among other things, sodium chloride. Test for the sodium by rubbing a clean, cold platinum wire over the palm of the hand, and hold in the flame.

Ammonium, NH_4^+

The **ammonium ion** behaves as if it were the ion of an alkali metal. In fact, amalgams of ammonium may be obtained by electrolyzing a solution containing ammonium ions, with the use of a mercury cathode. Like sodium and potassium, most of the ammonium salts are soluble. Picric acid yields yellow **ammonium picrate,** $NH_4OC_6H_2(NO_2)_3$. The perchlorate ion precipitates white **ammonium perchlorate,** NH_4ClO_4. **Sodium cobaltinitrite** produces a yellow precipitate of the corresponding ammonium salt, $(NH_4)_3Co(NO_2)_6$, with ammonium ion. Most of the common ammonium salts decompose or sublime on heating. Ammonium salts are used extensively as fertilizers.

Ammonia gas, NH_3, is extremely soluble in water, giving a solution that is basic in its reactions and that contains ammonium and hydroxyl ions in equilibrium with dissolved ammonia and ammonia vapor.

$$NH_4^+ + OH^- \rightleftharpoons \underset{\text{(dissolved)}}{NH_3} + H_2O \rightleftharpoons NH_{3_{\text{(vapor)}}}$$

Since heat usually decreases the solubility of gases in liquids, heating a solution of ammonium hydroxide will shift the equilibrium to the right and liberate ammonia gas. Strong bases, like potassium and sodium hydroxides, will also cause a shifting of the equilibrium to the right, displacing ammonia vapor.

PRELIMINARY EXPERIMENTS

1. Add dilute NaOH to a portion of NH_4^+ test solution, and warm gently. Test the vapors with moist litmus paper.
2. Heat some dry NH_4Cl strongly in a crucible. Hold a test tube filled with water in the vapors.
3. Treat a portion of the test solution with a saturated solution of picric acid.
4. Add some $HClO_4$ to another portion of the test solution.
5. To another portion add some freshly prepared $Na_3Co(NO_2)_6$ solution.
6. (*Optional*) Test the white dust that forms on acid bottles in the laboratory for the NH_4^+. What is this dust?

ANALYSIS OF GROUP V CATIONS

Outline of Separations

No group reagent is employed for the separation of the Group V cations. The ammonium ion is identified in a portion of the original

unknown solution. Magnesium is tested for in one portion of the filtrate from Group IV; the other portion of the solution is evaporated to dryness and ignited to remove ammonium salts. Tests are then made on separate portions of the ammonium-free solution for sodium and potassium ions.

Analytical Procedure

1. To a portion of the filtrate from Group IV, acid with HCl, add a drop of *p*-nitrobenzene-azo-resorcinol, and make strongly alkaline with NaOH.

Blue "lake" indicates **magnesium.**

Heat a second portion of the acid solution to boiling, and add Na_2HPO_4 solution. Treat the solution with a volume of dilute NH_4OH equal to one-third of the volume of the solution, and allow to cool.

White crystalline precipitate proves **magnesium.**

2. Evaporate the remainder of the Group IV filtrate to dryness, and ignite until no more fumes are evolved. Take up the residue in 2 ml. of water, and separate into two portions.

3. Treat a portion of the solution with 1 drop of an 0.05% solution of $AgNO_3$, and add some solid $Na_3Co(NO_2)_6$.

Yellow precipitate indicates **potassium.**

Perform a flame test on the solution, using several cobalt glasses.

Red-violet flame proves **potassium.**

4. To the second portion of the solution add some zinc uranyl acetate reagent.

Yellow precipitate indicates **sodium.**

Perform a flame test on either the solution or the precipitate.

Intense yellow flame proves **sodium.**

5. Treat a portion of the **original** unknown with an excess of NaOH, and warm gently. Test the vapors with moist litmus paper.

Odor of $\mathbf{NH_3}$ and red litmus turning blue proves $\mathbf{NH_4^+}$.

ANALYTICAL TABLE IX

Analysis of Group V

The filtrate from Analytical Table VIII may contain Mg^{++} K^+, and Na^+, and ammonium salts.

Test a portion of the **original unknown** for NH_4^+ with excess NaOH (**5**).

Make a portion of filtrate from Analytical Table VIII acid with HCl. Treat with *p*-nitrobenzene-azo-resorcinol, and make strongly alkaline with NaOH. Confirm Mg^{++} by the phosphate test (**1**).

Evaporate remainder of filtrate from Analytical Table VIII to dryness, and ignite. Take up residue in H_2O, and divide into two portions (**2**).

- Test one portion for K^+ with sodium cobaltinitrite. Confirm with flame test (**3**).
- Test second portion for Na^+ with zinc uranyl acetate reagent. Confirm with flame test (**4**).

ANALYTICAL TABLE X

Group Separation for General Unknown

Treat the not too strongly acid unknown with HCl until precipitation is complete. Filter.

Precipitate: Chlorides of Group I cations. Proceed as in Analytical Table I.

Filtrate: Groups II, III, IV, and V. Adjust the acidity, and saturate with H_2S. Filter.

- **Precipitate:** Group II sulfides. Proceed as in Analytical Tables II, III, and IV.
- **Filtrate:** (H_2S-free). Groups III, IV, and V. Make ammoniacal, add solid NH_4Cl, and saturate with H_2S. Filter, boil filtrate with glacial $HC_2H_3O_2$.
  - **Precipitate:** Sulfides and hydroxides of Group III. Proceed as in Analytical Tables V, VI, and VII.
  - **Filtrate:** Groups IV and V. Evaporate, treat with HCl several times, and evaporate to dryness. Dilute with H_2O, evaporate to dryness again, and dissolve residue in $0.2N$ HCl. Proceed as in Analytical Table VIII, using filtrate from last step for Group V analysis (Analytical Table IX).

CHAPTER XIV

INTRODUCTION TO BLOWPIPE ANALYSIS

Blowpipe analysis, which is truly a micro method, has long been known and used. In recent years, however, it has fallen into disuse. Nevertheless, the method has advantages that make its inclusion in an elementary course desirable. Blowpipe analysis is essentially a deductive method; *i.e.*, it is not generally feasible to group the ions systematically or to carry out individual separations, and the student must of necessity draw his conclusions from observations made on a limited number of tests. Since blowpipe unknowns contain both cations and anions, the deductive method is first applied to the cations, with whose chemistry the student is already familiar. Subsequently, it is applied to the detection of the simpler anions and so serves as an introduction to the purely deductive methods applied in the usual schemes of anion analysis.

The method has other marked advantages in a complete analysis of both simple and complex materials. First, it often enables the analyst to eliminate many specific ions and so shortens considerably the course of the analysis. Further, if the unknown is simple, it may be completely analyzed by this technique. The method also furnishes many excellent specific tests that, indeed, are frequently used even in the so-called wet analysis (cobalt bead test, Rinman's Green test for zinc, etc.).

The number of experiments in a preliminary analysis should be few, as should the number of reagents. Further, the complete examination should take only a short time. The few tests specified carry out this principle. It is, of course, possible to verify the presence of many substances by other methods, particularly those used in the wet method of analysis. However, the student is *strongly advised* to perform the blowpipe unknowns using *only* the reagents and experiments outlined in the following tables.

The tests used are:

1. Heating in a matrass.
2. Heating (*a*) on a charcoal block; (*b*) on a plaster of Paris tablet.
3. Borax and phosphate beads.
4. Flame tests.

5. Treatment with concentrated and dilute acids and alkali.

The various gases evolved and sublimates formed are usually further tested with simple reagents.

By extending this list, it is possible to do a complete analysis solely by blowpipe methods, as was frequently the case in the earlier days of qualitative analysis. However, the technique and knowledge of chemistry involved are generally beyond the capacity of the beginning student.

HEATING IN THE MATRASS

The matrass is a tube 3 to 4 in. long and 7 mm. outside diameter, having a bulb about 12 mm. in diameter at one end. Although a hard glass tube (Pyrex) is preferable, tubes made of soda-lime glass suffice. The student should make a number of these tubes. The bulb should not have too

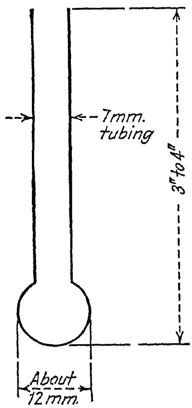


FIG. 53.—A matrass.

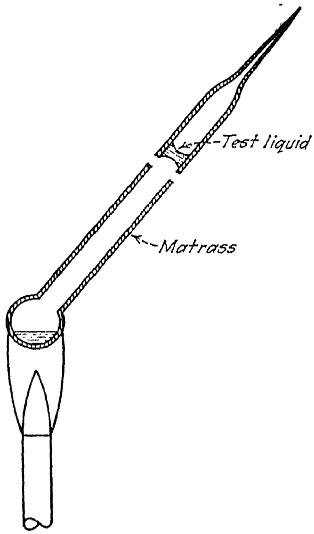


FIG. 54.—Testing for emergent gases.

heavy walls, and the glass in the bulb should be of equal thickness throughout.

A small amount of material is placed in the bulb and the tube heated in the flame. The following observations should be made:

1. Color of heated substance, hot and cold.
2. Condensation of vapors in the upper portion of tube.
3. Sublimates.
4. Evolution of gases, color, and odor.

ANALYTICAL TABLE XI
Heat in Matrass

Observation	Test	Indication
Decrepitation		$Pb(NO_3)_2$, NaCl and many other substances
Carbonization, with burned odor and H_2O		Organic matter, as tartrates
Water evolved	Action toward litmus: neutral	Hydrates, many hydroxides, free oxalic acid.
	Alkaline	Ammonium compounds
	Acid	Volatile acids
Gas evolved		
Colorless and odorless	Supports combustion—O_2	Some nitrates, chlorates, peroxides, iodates, certain oxides
	Burns with a blue flame—CO	Oxalates
	Turns baryta water bead turbid —CO_2	Carbonates, oxalates, organic matter
Colorless with characteristic odor	Alkaline to litmus—NH_3	Ammonium salts, some organic compounds
	Turns baryta water turbid. Bleaches $KMnO_4$—SO_2	Sulfur, sulfides, sulfites, some sulfates
	Turns lead acetate paper black —H_2S	Moist sulfides
	Acetone—recognized by odor	Acetates
	HCN—recognized by odor (CAUTION)	Cyanides
Colored with characteristic odor		
Red-brown	Starch—KI paper turns blue —NO_2	Nitrates of heavy metals; some nitrites
Reddish	Starch—KI paper turns blue —Br_2	Bromides in presence of oxidizing agents; bromides of some metals
Green	Starch—KI paper turns blue —Cl_2	Chlorides of some metals; chlorides in presence of oxidizing agents
Violet	Starch—KI paper turns blue—I_2	Iodides of some metals; iodides in presence of oxidizing agents
Sublimate forms		
White		Ammonium salts, Hg_2Cl_2, $HgCl_2$, As_2O_3, As_2O_5, Sb_2O_3
Yellow hot, white cold	(Note: may only be color of mass)	ZnO, Zn compounds
Yellow		As_2S_3, HgO (also globules of Hg), S from sulfides
Yellow	Turns red on rubbing	HgI_2
Black, with garlic odor		Many As compounds
Black, with violet fumes		Iodides in presence of oxidizing agents; some iodides
Gray to gray-black		Oxygen compounds of Hg, HgS

Testing of Emergent Gases.—In testing with liquid reagents, a drop of the liquid in the loop of a platinum wire, which is held over the mouth of the tube, may be used, A better method, however, is to seal one end of a small piece of tubing, introduce a drop of the reagent into the open end, and hold over the mouth of the tube.

Testing of the Residue.—The residue in the matrass may be obtained by breaking the tube.

NOTE: It is not practical to clean matrasses and reuse them.

ANALYTICAL TABLE XII

IN MATRASS WITH 3 TIMES THE WEIGHT OF ANHYDROUS COMMERCIAL Na_2CO_3

Observation	Test	Indication
Sharp odor.............	Alkaline to litmus—NH_3	All ammonium compounds
Gray mirror and globules.	Rub with filter paper and droplets form	Hg compounds
Gray metal (no globules) and garlic odor		As compounds

REDUCTION ON THE CHARCOAL

With a charcoal borer or a penknife, make a small, shallow depression in a charcoal block. Tamp into the depression a thorough mixture of 1 part of substance and 2 parts of anhydrous sodium carbonate. Heat in the blowpipe flame (using a blowpipe tip on the burner), holding the block in an inclined position.

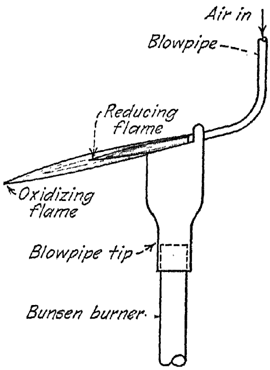


FIG. 55.—The blowpipe flame.

TECHNIQUE NOTES

1. Sometimes it is advantageous to place a layer of pure sodium carbonate over the mixture to keep it from blowing out of the cavity; or the mixture may be moistened with a drop of water.

2. With substances reduceable only with difficulty, it often helps to mix the fuse with powdered charcoal.

3. Heating usually should commence at the far side of the cavity, just outside of it, and the block should be gradually moved till the substance is in the direct blowpipe flame.

4. To observe sublimates, heat gently, and observe the parts of the charcoal that the flame has not touched. The parts of the charcoal the flame plays on will often have a gray-to-white deposit of ash on the surface, which must not be mistaken for a sublimate.

5. To test a metallic globule for malleability, clean the pellet, place it on the anvil, and strike with the hammer. A malleable particle will form a leaflet of metal; a brittle one will shatter.

6. In using the blowpipe, it is essential to learn to breathe at the same time that one is blowing into the blowpipe.

ANALYTICAL TABLE XIII

HEAT SUBSTANCE, WITH BLOWPIPE, ON A CHARCOAL BLOCK

Observation	Indication
Heated without Na_2CO_3	
Fuses and runs into charcoal	Salts of alkali metals
Decrepitates	NaCl, etc.
Deflagrates	Chlorates and nitrates
Infusible—residue moistened with H_2O is alkaline	Ba, Sr, Ca, Mg compounds
Residue + 1 drop of very dilute $Co(NO_3)_2$ solution, heated strongly, gives	
Blue mass	Al compounds
Green mass	Zn compounds
Pink mass	Mg compounds
Heated with Na_2CO_3	
Metallic globule without incrustation	
Yellow	Au salt
Red	Cu salt
White, malleable	Ag salt
Dissolve in a drop of HNO_3, add 1 drop of HCl: white curdy precipitate	
Metallic globule with incrustation	
Malleable globule	
Soluble in HNO_3	Pb salt
White ppt. with HNO_3	Sn salt
Brittle globule	
White incrustation	Sb compound
Yellow to white incrustation	Bi compound
No globule, only incrustation	
Yellow hot, white cold	Zn salt
White with garlic odor	As salt
Colored (see analytical table XIV)	
No incrustation	
Green mass	Cr compounds
Black mass (magnetic)	Fe, Co, Ni compounds
White glowing mass	Ca, Sr, Mg, Al compounds
Black mass	Sulfates, sulfides, thiosulfates, sulfites
Placed on silver coin and moistened, gives black stain (Hepar Test)	

IODIDE COATINGS ON PLASTER OF PARIS TABLETS

The plaster of Paris tablet should be prepared beforehand by spreading a ⅛- to ¼-in. layer of plaster of Paris on an oiled glass sheet or oiled Alberene table top. When set, the plaster of Paris layer is divided into 3- by 2-in. rectangles and then dried. The dry tablets are easily removed.

A shallow cavity is bored in the tablet, and a mixture of substance and "bismuth flux" (1 part KI and 1 part sulfur) is tamped into the cavity. The fuse is heated with the blowpipe flame.

Technique Notes

1. The degree of heating depends on the substance being examined. Some substances must be heated gently in the invisible cone of the blowpipe flame. Other substances should be heated very strongly.

ANALYTICAL TABLE XIV

Heat on Plaster Tablet with Bismuth Flux (KI + S)

Observation	Indication
Greenish yellow with brown both toward center and at distance; yellow with drop of $(NH_4)_2S_x$; nonvolatile	Cd compound
Chrome yellow; turns black when a drop of $(NH_4)_2S_x$ is added	Pb compound
Chocolate brown with underlying red; turns orange-yellow, then red when exposed to NH_3 fumes	Bi compound
Orange-red; disappears when exposed to NH_3 fumes	Sb compound

FUSIBLE BEADS ON THE PLATINUM WIRE

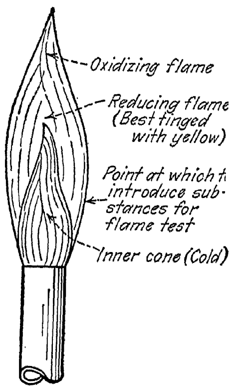


Fig. [illegible].—The Bunsen flame.

Clean the platinum wire by fusing some borax on it and then snapping off the molten flux. Repeat this until the bead that forms is clear and colorless. Make a clear bead on a loop in the platinum wire, and touch it, while hot, to a very small amount of the powdered substance. Reheat first in the oxidizing flame, then in the reducing flame. Observe the colors of the bead both hot and cold.

Technique Notes

1. After heating in the reducing flame, it is often useful to cool the bead in the reducing atmosphere existing in the cold inner cone of the Bunsen flame.

2. With substances that are oxidized only with difficulty, as MnO_2, the addition of a little potassium nitrate to the bead will aid the oxidation.

3. Only minute amounts of the substance should be fused in the bead. The intensity of the color varies with the concentration, and large amounts of substance often make the bead very dark and opaque.

ANALYTICAL TABLE XV

Bead Tests According to Elements*

Element		Borax bead		Microcosmic salt bead	
		Oxidizing	Reducing	Oxidizing	Reducing
Chromium...	Hot	Yellow	Green	Dirty green	Dirty green
	Cold	Yellowish green	Green	Fine green	Fine green
Iron.........	Hot	Deep yellow to orange-red	Bottle green	Deep yellow to brownish red	Red-yellow to yellow-green
	Cold	Yellow	Pale bottle green	Yellow to almost colorless	Almost colorless
Copper......	Hot	Green	Colorless to green	Green	Brownish green
	Cold	Blue	Opaque red with much oxide	Blue	Opaque red
Cobalt.......	Hot	Blue	Blue	Blue	Blue
	Cold	Blue	Blue	Blue	Blue
Nickel.......	Hot	Violet	Opaque gray	Reddish to brownish red	Reddish to brownish red
	Cold	Reddish brown	Opaque gray	Yellow to reddish brown	Yellow to reddish brown
Manganese...	Hot	Violet	Colorless	Grayish violet	Colorless
	Cold	Reddish violet	Colorless	Violet	Colorless
		Sodium carbonate bead—green or blue opaque in oxidizing flame; colorless in reducing flame			
Mixtures of Fe, Cu, Ni Co.	Hot	Green		Green	
	Cold	Yellow-green or blue		Yellow-green or blue	
Silicates......		Silica skeleton		Silica skeleton (most easily seen)	
Ag, Pb, Sb, Cd, Bi, Zn, Ni........			Opaque		Opaque

* Molybdenum, titanium, tungsten, uranium, and vanadium, which give colored beads, are not included in this table.

Color	Borax bead		Microcosmic salt bead	
	Oxidizing	Reducing	Oxidizing	Reducing
Opaque gray		h.c.—Ni, Ag, Pb, Sb, Cd, Bi, Zn		Ag, Pb, Sb, Cd, Bi, Zn, Ni
Violet	h.—Ni h.c.—Mn		h.c.—Mn	
Blue	c.—Cu h.c.—Co	h.c.—Co	h.c.—Co c.—Cu	h.c.—Co
Green	c.—Cr h.—Cu	h.c.—Cr, Fe h.—Cu	h.c.—Cr h.—Cu	h.c.—Cr h.—Fe, Cu
Yellow to brownish	h.—Cr, Ag h.c.—Fe c.—Ni		h.c.—Fe c.—Ni h.—Ag	h.—Fe c.—Ni
Red	h.—Fe c.—Ni	c.—Cu (opaque)	h.c.—Ni h.—Fe	c.—Cu h.c.—Ni

NOTE. h. = hot
c. = cold
h.c. = hot and cold

FLAME TESTS

Clean the platinum wire by heating in the Bunsen flame and by running concentrated hydrochloric acid over the wire from a capillary dropper and reheating until the wire gives no color in the flame. Touch the clean hot wire to some of the substance to be tested, and hold in the edge of the flame. Moisten with a drop of concentrated hydrochloric acid from the capillary dropper, and reheat.

TECHNIQUE NOTES

1. Some substances (notably sulfates) are nonvolatile in the Bunsen flame. Such substances should first be heated strongly in the reducing flame, then moistened with HCl and reheated.

2. In using a cobalt glass in testing for potassium, it is often advisable to use three or four thicknesses of glass.

ANALYTICAL TABLE XVII

Flame Colorations

Compounds	Coloration
Sodium	Yellow
Potassium	Violet (through two or three thicknesses of cobalt glass)
Calcium (volatile compounds, especially chlorides)	Orange to brick-red
Strontium	Crimson or carmine red
Barium	Yellowish (apple) green
Antimony	Pale greenish white
Copper halides	Blue or green
Bismuth	Pale greenish white
Lead	Pale azure tinged with green
	Bluish green (usually streaks or threads)
Boron (borates)	Green
Arsenic	Pale blue

TREATMENT WITH ACIDS OR ALKALI

A small amount of the substance is treated with the reagent in a small test tube. The color of any evolved gases is best observed against a white background.

ANALYTICAL TABLE XVIII

Gases Evolved on Treatment with Hydrochloric Acid

Gas evolved	Tests	Indication
CO_2	No odor; turbidity with baryta water	Carbonates
SO_2	Choking odor; bleaches drop of $KMnO_4$; turbidity with baryta water	Sulfites
SO_2 and ppt. of S		Thiosulfates
H_2S	Characteristic odor; lead acetate paper turns black	Sulfides
NO_2	Brown gas with characteristic odor; starch-KI paper turns blue	Nitrites
HCN	**CAUTION:** bitter almond odor	Cyanides

ANALYTICAL TABLE XIX

Gases Evolved with NaOH Solution and Heat

NH_3	Distinctive odor; turns litmus blue	Ammonium salts; some organic nitrogen compounds

ANALYTICAL TABLE XX

TREATMENT WITH COLD CONCENTRATED H_2SO_4

Observation	Tests	Indication
Vapor evolved		
Colorless and odorless.	CO_2—turns baryta water turbid	Carbonates and oxalates
	CO—burns with blue flame (no blackening)	Oxalates
Colorless with characteristic odor.	Acid vapor—turns litmus red	Volatile acids
	Fumes when breath is blown across tube	Halogen acids
	Vinegar odor	Acetates
	Burned odor; blackening of solution, SO_2	Organic matter, tartrates*
	Turns water bead turbid; etches glass	Fluorides and fluosilicates
	Bleaches $KMnO_4$ bead; returns baryta water turbid	Sulfites, thiosulfates, reducing agents on H_2SO_4
Characteristic odor and color		
Yellowish green.....	Bleaches litmus; turns starch-KI paper blue—Cl_2	Chloride and oxidizing agent together
Yellow.......	Explosive; sweet odor **CAUTION:** ClO_2	Chlorates
Brown to red.	Chromyl chloride—CrO_2Cl_2	Chromates and chlorides
	Br_2—usually mixed with HBr, SO_2, and H_2S, (test for HBr); starch-KI paper	Bromides
	NO_2—starch-KI paper	Nitrates, nitrites
Violet.	Condenses on upper part of tube—I_2	Iodides

* NOTE: It is advisable to warm the solution slightly at times, especially in the test for tartrates.

CHAPTER XV

ANION ANALYSIS

GROUP I ANIONS

CARBONATE, $CO_3^{=}$

Carbonic acid, H_2CO_3, does not exist as such but is essentially a solution of carbon dioxide in water. Salts of the acid are found widely distributed on the earth's surface as limestone, dolomite, marble, chalk, and as components of stalactitic and stalagmitic growths in underground caverns. Soluble carbonates cause water hardness. The gas, CO_2, is widely distributed in the atmosphere, being essential for plant photosynthesis.

The carbonates, which may be obtained by passing carbon dioxide through a solution of a metallic hydroxide, are generally insoluble, with the exception of the **alkali metal salts.** They undergo hydrolysis and form alkaline solutions:

$$CO_3^{=} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

A number of carbonates, particularly those of the **alkaline earth metals,** react with excess CO_2 in aqueous solution, forming the soluble bicarbonate ion, HCO_3^- (primary carbonate ion). The reaction may be reversed by boiling the solution, whereupon CO_2 is driven off, and the normal (secondary) carbonate is reprecipitated.

Bicarbonates also hydrolyze to give an alkaline solution:

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

but the hydrolysis proceeds to a lesser extent than with the carbonates. The alkalinity produced by the hydrolysis of carbonates is detectable with phenolphthalein, whereas that of the bicarbonate hydrolysis is not.

Carbonates decompose with effervescence when treated with **mineral acids** because of the evolution of CO_2. The gas is colorless and odorless and may be recognized by the turbidity produced when it is passed into **barium hydroxide** solution. The disappearance of the suspension of $BaCO_3$ when a large amount of CO_2 is used is due to the formation of $Ba(HCO_3)_2$.

Barium or calcium chloride precipitates the corresponding white carbonate from normal (secondary) carbonate solutions. The

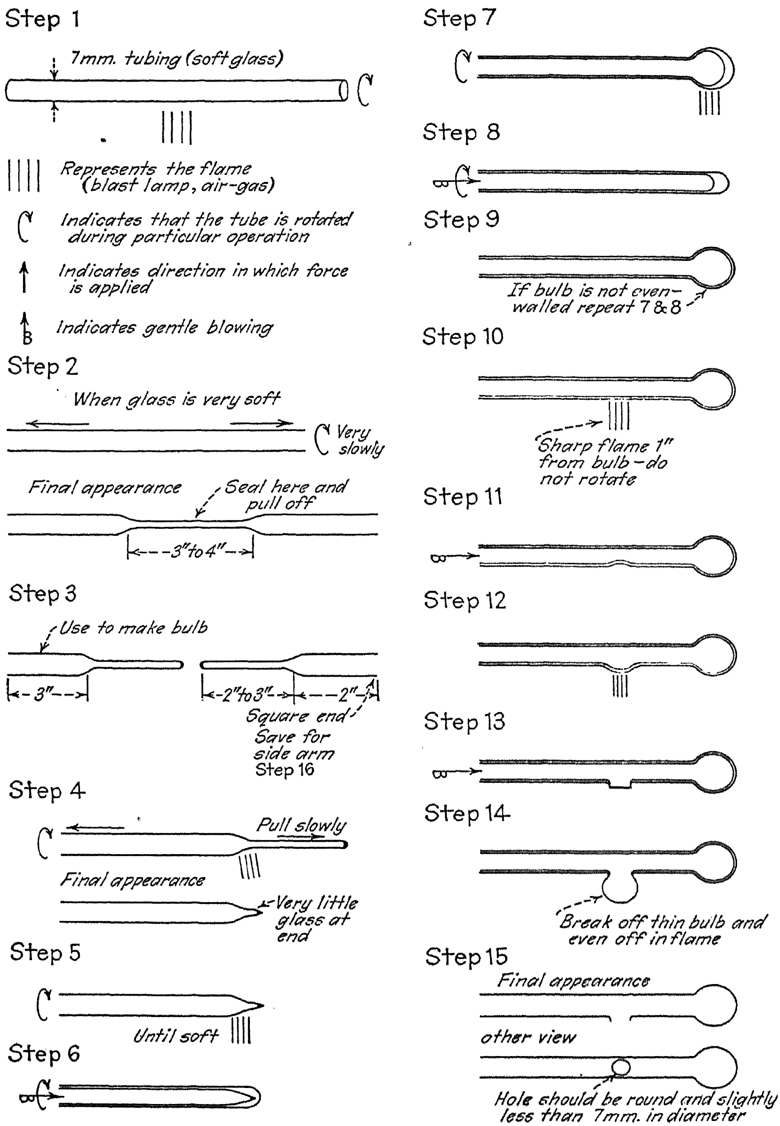


FIG. 57.—Steps in making a micro gas generator.

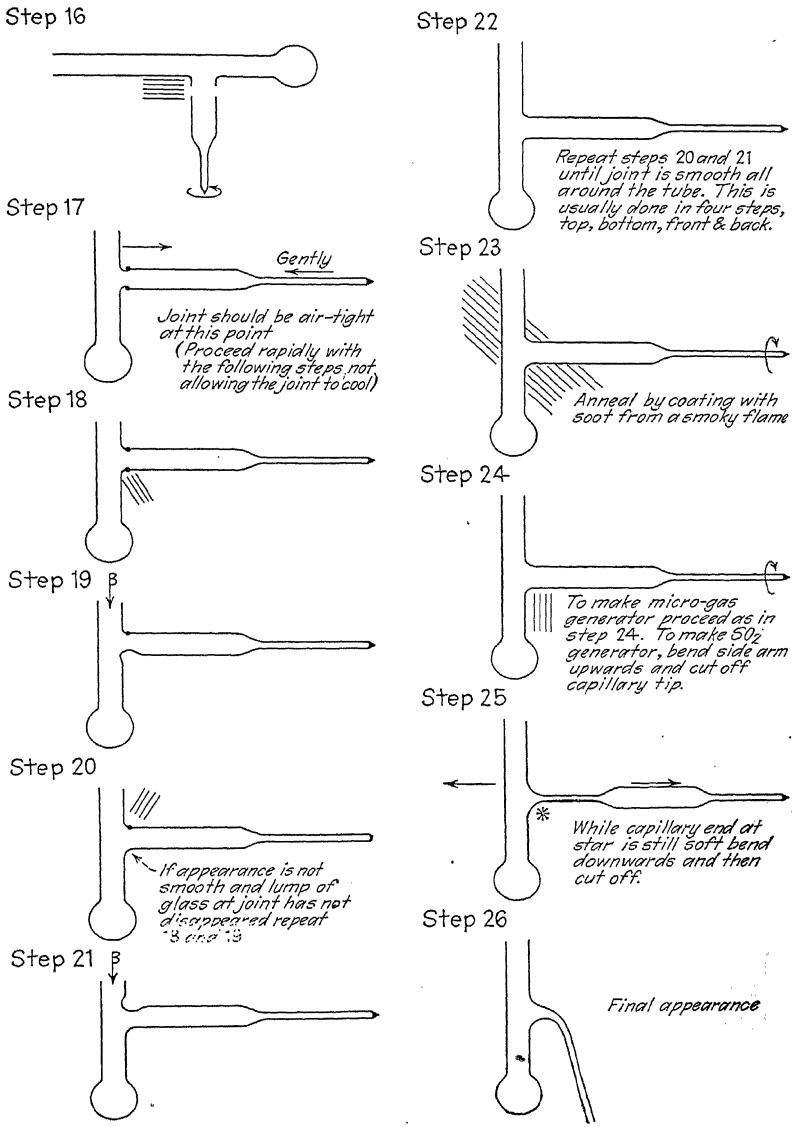


FIG. 57.—(*Continued.*)

precipitates are soluble in mineral acids and in excess carbon dioxide. **Barium carbonate** is soluble in dilute (30%) acetic acid, which distinguishes it from **barium sulfite.** Silver nitrate precipitates white **silver carbonate,** Ag_2CO_3, which turns yellow with an excess of reagent; on boiling, the precipitate turns brown because of decomposition into Ag_2O and carbon dioxide.

PRELIMINARY EXPERIMENTS

1. Cautiously add dilute HCl to a small amount of concentrated Na_2CO_3 solution. Prepare a micro gas generator, as illustrated in Figs. 57 and 58. Place a small amount of solid Na_2CO_3 into the bulb,

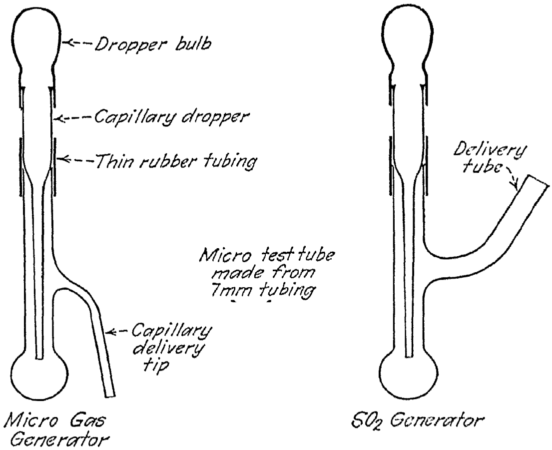


FIG. 58.—Assembled gas generator.

and fill the dropper with dilute HCl. Add a few drops of acid to the salt, and collect the gas in a few drops of $Ba(OH)_2$ solution. Continue until an excess of CO_2 has been added. Boil the resulting solution.

2. Treat a portion of solid Na_2CO_3 in the generator with dilute HCl. Pass the gas into $Ba(OH)_2$ solution. Ascertain the solubility of the precipitate in 30% acetic acid.

3. Add a drop of phenolphthalein to a few drops of an 0.01*N* solution of Na_2CO_3. Repeat the test with an 0.01*N* $NaHCO_3$ solution. Saturate the Na_2CO_3 solution with CO_2, using the microgas generator.

SULFITE, SO_3

Sulfurous acid, H_2SO_3, is, in the main, an aqueous solution of sulfur dioxide. The solution undergoes auto-oxidation and reduction at room

temperature, forming sulfuric acid and free sulfur. The gas, SO_2, is widely used as a preservative for dried fruits, as a refrigerant, as a disinfectant, as an aid in the conversion of wood pulp into paper, and in the commercial manufacture of sulfuric acid.

The **alkali metal sulfites** are soluble in water; all the others are slightly soluble to insoluble. Since sulfurous acid is dibasic, it also forms acid (primary) salts, the **bisulfites,** most of which are soluble in water. Sulfurous acid and the sulfites are readily oxidized in air or by oxidizing agents and are therefore considerably used as reducing agents and as bleaches where reducing action is desired.

Sulfites decompose readily when treated with **mineral acids,** giving off sulfur dioxide, which has a suffocating, pungent odor. The gas decolorizes **potassium permanganate** solution, undergoing oxidation to sulfate ion in the process. Sulfurous acid will also decolorize **iodine solution,** reduce **arsenate** to arsenite, **dichromate** ion to chromic ion, and **ferric** to ferrous ion. With **sodium nitroprusside,** $Na_2Fe(CN)_5NO$, and zinc sulfate (**zinc nitroprusside**) and ammonia vapors, sulfur dioxide produces a purplish-red coloration. With Ba^{++}, sulfites form white **barium sulfite,** $BaSO_3$, which is insoluble in 30% acetic acid. Strontium ion yields **strontium sulfite,** which is very slightly soluble in water. This fact is used in separating sulfite from thiosulfate.

PRELIMINARY EXPERIMENTS

1. Treat a small portion of solid Na_2SO_3 in a generator with dilute HCl. Pass some of the gas into a very dilute solution of $KMnO_4$, acidified with 1 drop of dilute H_2SO_4. Repeat the experiment, using a dilute iodine solution in place of the $KMnO_4$.

2. Place small amounts of solid Na_2SO_3 in each of three test tubes. Add 3% H_2O_2 to the first, K_2CrO_4 solution to the second, and a few drops of bromine water to the third tube. After 5 min., treat each solution with dilute HCl, and note whether any gas is evolved.

3. Place some solid Na_2SO_3 in the bulb of a gas generator that has the side arm bent upward (Fig. 58). Fill the dropper with dilute HCl, and place a wood splint coated with zinc nitroprusside in the side arm. Add a few drops of acid to the solid, and heat on a sand bath for about 5 min. Remove the splint, and hold it over an open bottle of NH_4OH. This test is interfered with by sulfide.

4. Treat a portion of solid Na_2SO_3 in the generator with dilute HCl. Pass the gas into $Ba(OH)_2$ solution. Ascertain the solubility of the precipitate in 30% acetic acid.

5. Add $SrCl_2$ solution to a portion of $SO_3^=$ test solution.

THIOSULFATE, $S_2O_3^{=}$

Free thiosulfuric acid, $H_2S_2O_3$, is unknown because of its instability. Except for the salts of the **alkali metals,** all the thiosulfates are insoluble or are only sparingly soluble in water. Acidification of an aqueous solution of a thiosulfate results in the precipitation of sulfur after a short time, together with the evolution of sulfur dioxide.

Sodium thiosulfate, $Na_2S_2O_3$, is the most important salt. This was formerly and often still is called sodium hyposulfite. This name is incorrect, although the term hypo is still used by photographers. It is used extensively as a solvent for unchanged silver halides in the "fixing" of photographic film, yielding the complex ion, $[Ag_2(S_2O_3)_3]^{\equiv}$. **Alkali thiosulfates** dissolve many water-insoluble compounds with the formation of complex salts. Lead sulfate, calcium sulfate, the silver halides, mercurous chloride, lead iodide, and other substances react in this fashion.

Thiosulfates are fairly strong reducing agents. **Potassium permanganate,** in acid solution, is reduced to Mn^{++} by $S_2O_3^{=}$, which, in turn, is oxidized to sulfate ion. The visual reaction is a decoloration of the solution. **Ferric ion** and $\mathbf{Cr_2O_7^{=}}$ are also reduced by this anion to ferrous ion and chromic ion, respectively.

Silver ion forms a white precipitate of **silver thiosulfate,** $Ag_2S_2O_3$, which, on standing, becomes yellow, then brown and finally black, because of the formation of silver sulfide, Ag_2S:

$$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4$$

When an excess of $S_2O_3^{=}$ is present, the complex ion $[Ag_2(S_2O_3)_3]^{\equiv}$ is obtained, which, on dilution and boiling, yields $S_2O_3^{=}$, $SO_4^{=}$, SO_2, S, and Ag_2S. **Strontium chloride,** in faintly alkaline solution that is not too concentrated, gives no precipitate with thiosulfate, in contrast with sulfite ion.

When $S_2O_3^{=}$ is added to a mixture of **sodium azide,** NaN_3, **and iodine,** it functions as a catalytic agent, causing the two latter substances to react, and bubbles of nitrogen gas are evolved. Only sulfide and thiocyanate interfere with this test.

PRELIMINARY EXPERIMENTS

1. Add dilute HCl to a freshly prepared concentrated solution of $Na_2S_2O_3$.

2. Mix equal volumes of $S_2O_3^{=}$ test solution and $0.1N$ $KMnO_4$ solution. Acidify with dilute H_2SO_4.

3. To 0.5 ml. of Ag^+ test solution, add $S_2O_3^{=}$ solution, drop by drop, until the precipitate that first forms redissolves. Heat the solution on a water bath for a short time.

4. Seal off one end of a 1-in. length of 5-mm. glass tubing. Place some NaN_3-I_2 reagent in the tube, and clamp it in a vertical position with the sealed end at the top. Moisten a platinum wire with distilled water, dip into finely powdered $Na_2S_2O_3$ and introduce into the reagent.

5. Add $SrCl_2$ solution to a portion of $S_2O_3^=$ test solution. Compare with the same test under Sulfite.

Sulfide, $S^=$

Hydrogen sulfide, H_2S, is a colorless gas with a characteristic "rotten egg" odor. It is partially soluble in water, giving a feebly acidic reaction. All the hydrogen sulfide is readily expelled when the aqueous solution is heated. The gas, when inhaled, is toxic, and since it is used extensively in the laboratory as a precipitant for many of the cations, *care should always be exercised in its use.*

The sulfides of the **alkali metals** are readily soluble in water; all the others, with a few exceptions, are insoluble. The soluble salts are hydrolyzed with the evolution of H_2S and the production of an alkaline solution. The sulfides of the alkaline earth metals, which are only slightly soluble, hydrolyze to form the acid sulfides, which are quite soluble in water. The sulfides of Al^{+++}, Mg^{++}, and Cr^{+++} do not exist in aqueous solution.

Sulfide ion, in both acid and alkaline mediums, is a strong reducing agent. **Nitric acid** is reduced to nitric oxide, NO, and $S^=$ is oxidized to free sulfur; **$KMnO_4$ solution** is bleached by H_2S, with the formation of Mn^{++} and the separation of free sulfur.

The characteristic odor of H_2S is a good indication of its presence. A piece of filter paper moistened with $\mathbf{Pb(C_2H_3O_2)_2}$ solution turns black on exposure to H_2S because of the formation of PbS. The use of sodium plumbite, Na_2PbO_2, is believed to give a more delicate test. The sulfide ion catalyzes the reaction between **sodium azide and iodine** to evolve nitrogen gas (see Thiosulfate). Alkaline solutions of $S^=$ give an intense violet coloration with **sodium nitroprusside,** $Na_2Fe(CN)_5NO$.

PRELIMINARY EXPERIMENTS

1. Treat a small crystal of Na_2S with dilute HCl. Repeat, holding a strip of $Pb(C_2H_3O_2)_2$ paper over the mouth of the tube.

2. Repeat the NaN_3-I_2 test described under Thiosulfate, substituting Na_2S for the $Na_2S_2O_3$.

3. Place several drops of Na_2S solution on a spot plate, and make slightly alkaline with dilute NaOH. Add a drop of sodium nitroprusside reagent.

4. Saturate 5 ml. of H_2O with H_2S, and add a few drops of the solution to each of the following reagents: $FeCl_3$, K_2CrO_4, $KMnO_4$, HNO_3 (dilute and concentrated).

5. (*Optional*) Take 1 ml. of a saturated solution of H_2S, and determine how much it may be diluted and still give a brown coloration with Na_2PbO_2 solution. [The latter may be prepared by adding NaOH to $Pb(NO_3)_2$ until the precipitate formed redissolves.]

CYANIDE, CN^-

Hydrocyanic acid, HCN, is a clear, colorless liquid having a low boiling point (26.5°C.). It has an odor of bitter almonds and is extremely poisonous. The acid may be obtained by acidification of cyanide salts. It is readily soluble in water and hydrolyzes completely, on standing, into **ammonium formate,** $HCOONH_4$. It is an extremely weak acid, **carbon dioxide** liberating HCN from its salts. Hydrocyanic acid is used as a fumigant. It occurs naturally in the glycoside (amygdalin) of oil of bitter almonds.

The acid and salts are extremely poisonous, and care must be exercised in their use. The cyanides of the **alkali, alkaline earth metals,** and **mercuric mercury** are water-soluble; all the others are insoluble. A number of these insoluble heavy metal cyanides are soluble in an excess of CN^-, with the formation of complex ions. This tendency is especially characteristic of cyanide ion and is utilized in the recovery of gold and in electroplating. The ferro- and ferricyanides, $[Fe(CN)_6]^{\equiv}$ and $[Fe(CN)_6]^{=}$, are the most common examples of this type of complex formation. They are utilized in detecting CN^- by the formation of Prussian Blue (ferri-ferrocyanide), $Fe_4[Fe(CN)_6]_3$.

Cyanides may also be converted to thiocyanate, CNS^-, by heating with **ammonium polysulfide.** The CNS^- is then identified as the blood-red ferrithiocyanate complex, $Fe(CNS)^{++}$. This test is extremely sensitive and is suitable for detecting CN^- in the atmosphere. When a mixture of **copper acetate and benzidine acetate** is exposed to the vapors of HCN, a blue coloration is produced through the oxidation of the benzidine.

PRELIMINARY EXPERIMENTS

(*This section may be omitted at the discretion of the instructor*)

1. Treat a portion of CN^- test solution with dilute HCl. Fan some of the vapors toward the nose, and smell cautiously. (**CAUTION: NEVER** smell HCN directly. Dilute with air by proceeding as directed.)

2. Add some $FeSO_4$ solution, and dilute NaOH to a portion of the CN^- test solution. Heat to boiling, acidify with dilute HCl, and add several drops of $FeCl_3$ solution.

3. To a small volume of CN^- solution add some $(NH_4)_2S_x$, and heat on the water bath until a clear solution is obtained. Make the solution faintly acid with dilute HCl, and add a few drops of $FeCl_3$ solution.

4. Place 0.5 ml. of the test solution in a porcelain crucible, add several drops of dilute H_2SO_4, and cover the crucible tightly with a piece of filter paper. Moisten the paper with a drop of a previously mixed solution of $Cu(C_2H_3O_2)_2$ (2 g./liter) and benzidine acetate.

Nitrite, NO_2^-

The free acid, HNO_2, has never been isolated and exists only in solution. The latter may be prepared by acidifying a cold solution of a nitrite with dilute sulfuric acid. The aqueous solution, pale blue in color, decomposes to give nitric oxide, NO, nitric acid, HNO_3, and water. The first product oxidizes in air to give brown fumes of NO_2.

All the **nitrites** are readily soluble in water with the exception of the silver salt, $AgNO_2$, which is only sparingly soluble. Nitrites function readily as both oxidants and reductants. The anion easily oxidizes **sulfide** to sulfur, **ferrous** to ferric ion, **iodide** to iodine, and **ammonium** ion to nitrogen. Many other examples are known. In **acid solution,** NO_2^- reduces all the common oxidizing agents, MnO_4^-, $Cr_2O_7^=$, and ClO_3^-. The anion, in turn, is readily oxidized to nitric acid. Nitrites form complex ions with a number of cations like cobaltic, ferrous, and cupric ions. The most important of these is the cobaltinitrite (hexanitritocobaltate) ion, $[Co(NO_2)_6]^{\equiv}$.

When solutions of nitrite ion are treated with sulfuric acid and a crystal of $FeSO_4$, a **brown ring** is produced (see Nitrate). Addition of NO_2^- to an acid solution of **brucine sulfate** produces an intense red coloration. Solutions of nitrous acid have the property of reacting with **organic bases** (**amines**), producing compounds that will react or "couple" with certain other organic compounds to form colored substances and dyes. Treatment of an acetic acid solution of **naphthylamine** with $NaNO_2$ solution and **sulfanilic acid** solution produces a deep red coloration. This is a very sensitive test for nitrite ion (Peter Griess test).

PRELIMINARY EXPERIMENTS

1. Treat a small amount of solid $NaNO_2$ with dilute HCl or H_2SO_4. Repeat the test, holding a strip of starch-KI paper in the escaping fumes.

2. Place several drops of $NaNO_2$ solution on a spot plate, and add a small crystal of $FeSO_4$. Allow an equal volume of concentrated H_2SO_4 to flow down the side of the depression.

3. Dissolve a minute amount of brucine (**CAUTION**) in a few drops of concentrated H_2SO_4, and add a drop of NO_2^- solution.

4. *Peter Griess Test.*—Place several drops of $NaNO_2$ solution on a spot plate, and add an equal volume of dilute acetic acid. Treat the solution with a slight excess of a previously mixed solution of naphthylamine and sulfanilic acid.

ANALYSIS OF GROUP I ANIONS

1. Group Reagent.—Dissolve a portion of the unknown in water and treat with dilute HCl. Warm gently. Note the odor (**CAUTION**), and test the escaping gases with starch-KI paper and with lead acetate paper. Nitrite is indicated if the starch-KI paper turns blue, and the characteristic black precipitate of PbS and an odor of H_2S indicate sulfide. The deposition of free sulfur and an odor of SO_2 imply the presence of thiosulfate. A bitter almond odor indicates cyanide.

2. Reducing Acids.—Make two ml. of the unknown solution acid with dilute H_2SO_4. Dilute to 5 ml., and then add 0.5 ml. of dilute H_2SO_4 in excess. Treat with several drops of 0.1*N* $KMnO_4$. Bleaching of the reagent indicates the presence of one or more of the following: sulfite, thiosulfate, sulfide, and nitrite. The following tests are applied if the tests given above indicate that certain anions may be present.

3. Cyanide.—Place about 0.5 ml. of the unknown solution in the gas generator, add 40 mg. $BaCl_2$, 120 mg. of $NaHCO_3$, warm, and collect the gas evolved in dilute NaOH. Add $FeSO_4$ solution to the NaOH solution, heat to boiling, acidify with dilute HCl, and treat with several drops of $FeCl_3$ solution.

Blue coloration or precipitate proves **cyanide.**

4. Carbonate in the Presence of Sulfite and Thiosulfate.—Place some of the unknown in a gas generator, treat with dilute HCl, and pass the gas into $Ba(OH)_2$ solution contained in a second gas generator. A white precipitate indicates carbonate, sulfite, or thiosulfate, alone or in combination. Wash the precipitate, remove the wash water, add a few drops of 30% acetic acid, and pass the gas into a tube of $Ba(OH)_2$ solution.

White precipitate proves **carbonate.**

5. Sulfide.—Dissolve a portion of the original unknown in water, and treat part of the solution with dilute HCl. Place a piece of $Pb(C_2H_3O_2)_2$ paper in the escaping fumes.

Black precipitate of PbS indicates **sulfide.**

Place a few drops of the original solution on a spot plate, and make slightly alkaline with dilute NaOH. Treat with a drop of sodium nitroprusside reagent.

Intense violet coloration proves **sulfide.**

If $S^{=}$ is present, treat the concentrated unknown solution with solid $CdCO_3$. Shake, and filter off the excess $CdCO_3$ and CdS that forms. Reserve the filtrate for step 6.

6. Sulfite.—Add some $1N$ $SrCl_2$ solution to a neutral or faintly alkaline solution of the original solution or to the filtrate from step 5, if $S^{=}$ is present. Warm, and allow the solution to stand for about 10 min. A white precipitate indicates carbonate or sulfite. Filter and reserve the filtrate for step 7. Place the precipitate in a gas generator with the side arm bent upward, and place a wooden splint coated with zinc nitroprusside in the side arm. Treat the precipitate with dilute HCl, and heat on a sand bath for about 5 min. Remove the splint, and hold it over an open bottle of NH_4OH.

Purple coloration proves **sulfite.**

7. Thiosulfate.—Treat the filtrate from step 6 with dilute HCl.

Odor of SO_2 and precipitate of S proves **thiosulfate.**

8. Nitrite.—If a colored gas was obtained in step 1 and a positive reaction was obtained with starch-KI paper, apply the following test: Dissolve some of the unknown in water, place a few drops on a spot plate, and add an equal volume of acetic acid. Treat with a slight excess of a previously mixed solution of naphthylamine and sulfanilic acid.

Deep red coloration proves **nitrite.**

GROUP II ANIONS

Fluoride, F^-

Fluorides are found in nature as fluorite, CaF_2, cryolite, Na_3AlF_6, and in many silicates. Fluorides in small amounts are essential for human metabolism. When larger amounts are ingested, as in certain drinking waters, they cause mottling of the teeth. Sodium fluoride,

NaF, is used as insecticide and rodent exterminator. Organic fluoro compounds (freon) are used as refrigerants in some makes of electric refrigerators.

Although anhydrous **hydrofluoric acid,** H_2F_2, is sold commercially, the most common commercial form is the 40% aqueous solution, which must be kept in ceresin or wax bottles. The acid is very corrosive to the skin and gives very painful burns. Hydrofluoric acid is unique in that it will readily react with (etch) **glass, silica,** and **silicates** to form a gas, **silicon tetrafluoride,** SiF_4, which reacts with water to give **silicic acid,** H_4SiO_4, and **fluosilicic acid,** H_2SiF_6. Concentrated **sulfuric acid** liberates the free acid from fluorides.

Among the metallic salts, **silver fluoride,** AgF, is soluble in water. **Barium fluoride,** BaF_2, is soluble in an excess of mineral acid and in ammonium salts. Calcium ion precipitates white, slimy **calcium fluoride,** CaF_2, which is difficultly soluble in hydrochloric acid and almost insoluble in acetic acid.

PRELIMINARY EXPERIMENTS

1. Add an excess of $BaCl_2$-$CaCl_2$ reagent to 1 ml. of NaF solution. Treat the precipitate with dilute HCl. Treat another portion with dilute acetic acid.

2. Place a small amount of calcium fluoride in a clean lead dish and add enough concentrated H_2SO_4 to make a thin paste. Cover with a soft glass slide or glass plate that has been coated with paraffin, through which several characteristic symbols have been scratched. Let stand overnight.

3. In a test tube, place a mixture of calcium fluoride and pure quartz sand. Add concentrated H_2SO_4, and heat. In the mouth of the tube, place a glass tube closed at the upper end, containing a drop of water at the lower end.

SULFATE, $SO_4^{=}$

Sulfuric acid, H_2SO_4, is one of the basic substances of industry. Although it is made from native sulfur, many sulfates are found in nature as gypsum, $CaSO_4 \cdot 2H_2O$, barite, $BaSO_4$, and celestite, $SrSO_4$. The acid is used in industry whenever a cheap, strong acid is desired. The concentrated acid is a very strong dehydrating agent.

From solutions containing $SO_4^{=}$, Ba^{++} precipitates white **barium sulfate,** $BaSO_4$, which is insoluble in all acids. **Calcium sulfate,** $CaSO_4$, is, however, slightly soluble in water. With concentrated solutions of $SO_4^{=}$, Ag^+ precipitates white **silver sulfate,** Ag_2SO_4, (solubility, 0.58 g./100 ml. H_2O at 18°C.). With Pb^{++}, white **lead sulfate,** $PbSO_4$,

is precipitated, which is soluble in concentrated ammonium acetate solution.

Sulfates, like all other sulfur compounds, when fused with sodium carbonate and charcoal, yield sulfides (Hepar test). Barium sulfate, with mercuric nitrate solution, gives a yellow absorption compound.

PRELIMINARY EXPERIMENTS

1. Add an excess of $BaCl_2$-$CaCl_2$ reagent to 1 ml. of Na_2SO_4 solution. Treat the precipitate with dilute HCl.

2. *Hepar Test.*—Mix thoroughly small amounts of a solid sulfate, anhydrous Na_2CO_3 and powdered charcoal. Place in a cavity in a charcoal block and heat with a blowpipe flame. Place the black fused mass on a silver coin and moisten with a drop of water.

3. To a solution of Na_2SO_4 add excess $Pb(C_2H_3O_2)_2$ solution. Treat the precipitate with hot saturated ammonium acetate solution.

4. To a small portion of barium sulfate on a watch glass add 5 drops of mercuric nitrate reagent, and warm gently.

PHOSPHATE, $PO_4^{\equiv}$

Phosphorus forms several series of acids, the most important being the metaphosphoric acid, HPO_3, pyrophosphoric acid, $H_4P_2O_7$, and orthophosphoric acid, H_3PO_4, in all of which phosphorus has a valence number of 5. These acids are derived from P_2O_5 by the addition of varying amounts of water:

$$P_2O_5 + H_2O \rightarrow 2HPO_3$$
$$P_2O_5 + 2H_2O \rightarrow H_4P_2O_7$$
$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

The acid most commonly encountered is orthophosphoric acid, which is the only one considered in this analytical scheme.

Orthophosphoric acid forms three series of salts differing in the number of atoms of hydrogen replaced. For instance, the three sodium salts would be primary sodium orthophosphate, NaH_2PO_4, secondary sodium orthophosphate, Na_2HPO_4, and tertiary sodium orthophosphate, Na_3PO_4. A water solution of the **primary salt** is acid to methyl orange and phenolphthalein. The **tertiary salt** is basic to both indicators; the **secondary salt** is basic to methyl orange and acid to phenolphthalein.

Orthophosphoric acid is very important, inasmuch as in the form of tertiary calcium phosphate it is the main component of the bones of vertebrates. Phosphorus is widely distributed in nature in soils and

in plants and also occurs in the minerals calcium phosphate and apatite. It is a common constituent of fertilizers.

With Ag^+, in neutral solution, yellow **silver phosphate,** Ag_3PO_4, is precipitated that is readily soluble in nitric acid and ammonium hydroxide. With Ba^{++}, white amorphous **secondary barium phosphate,** $BaHPO_4$, is precipitated. However, in the presence of NH_4^+, **tertiary barium phosphate,** $Ba_3(PO_4)_2$, is obtained. Both barium phosphates are soluble in mineral and acetic acids. Ammonium molybdate, $(NH_4)_2MoO_4$, in excess, slowly precipitates yellow crystalline **ammonium phosphomolybdate,** $(NH_4)_3PO_4 \cdot 12MoO_3$, from nitric acid solution. Ferric ion precipitates yellow-white **ferric phosphate,** $FePO_4$, insoluble in acetic acid. Magnesia mixture (NH_4Cl, NH_4OH and $MgCl_2$) precipitates white crystalline **magnesium ammonium phosphate,** $MgNH_4PO_4$, which is soluble in acids.

PRELIMINARY EXPERIMENTS

1. Add an excess of $BaCl_2$-$CaCl_2$ reagent to 1 ml. of Na_2HPO_4 solution. Treat the precipitate with dilute HCl.
2. Treat separate portions of primary, secondary, and tertiary sodium phosphate solutions with methyl orange and phenolphthalein indicators.
3. Add a large excess of magnesia mixture to an ammoniacal solution of a phosphate. To the precipitate add dilute HCl.
4. To a phosphate solution, acid with nitric acid, add a large excess of ammonium molybdate reagent, and heat to 50°C.
5. To secondary phosphate test solution, add a slight excess of $AgNO_3$ solution. Treat the precipitate with dilute HNO_3.
6. To a solution of sodium phosphate, add $FeCl_3$ solution. Treat the precipitate with acetic acid.

ARSENATE, AsO_4^{-3}

There are three arsenic acids, corresponding to the three phosphoric acids; meta-arsenic acid, $HAsO_3$, pyroarsenic acid, $H_4As_2O_7$, and orthoarsenic acid, H_3AsO_4. Both the meta and pyro acids react with water to give the ortho acid whose salts are, therefore, the most common.

Arsenates yield white **barium arsenate,** $Ba_3(AsO_4)_2$, when treated with barium salts. The precipitate is soluble in dilute acids. When hydrogen sulfide is passed into a cold $0.3N$ acid solution of an arsenate, no precipitation occurs immediately, although after a long time, **arsenous sulfide,** As_2S_3, is precipitated. However, if the solution contains a large excess of hydrochloric acid, yellow **arsenic penta-**

sulfide, As_2S_5, is precipitated. If the hydrogen sulfide is passed into a hot strongly acid solution of an arsenate, a mixture of arsenous and arsenic sulfides is obtained. Arsenate is reduced to **arsenite** by **sulfurous acid. Magnesia mixture** ($MgCl_2$, NH_4Cl, and NH_4OH) precipitates white **magnesium ammonium arsenate,** $MgNH_4AsO_4$, which is soluble in acids. A large excess of **ammonium molybdate,** $(NH_4)_2MoO_4$, precipitates, from boiling nitric acid solution of arsenate, yellow crystalline **ammonium arsenomolybdate,** $(NH_4)_3AsO_4 \cdot 12MoO_3$, which is soluble in ammonium hydroxide and alkalis. **Iodide ion,** in strongly acid (HCl) solution, reduces arsenate to arsenite, with the liberation of free iodine. Silver ion precipitates chocolate-brown **silver arsenate,** Ag_3AsO_4 (see Arsenic, pages 177*ff.*).

Arsenite, AsO_2^-

There are three arsenous acids: meta-arsenous acid, $HAsO_2$, pyroarsenous acid, $H_4As_2O_5$, and orthoarsenous acid, H_3AsO_3. The salts of the meta acid are those most commonly encountered, although orthoarsenite ion exists in solution.

Barium ion precipitates, from solutions of arsenite, white **barium arsenite,** $Ba(AsO_2)_2$, which is soluble in dilute acids. Hydrogen sulfide precipitates yellow **arsenous sulfide** from acid solutions of arsenite. Yellow **silver orthoarsenite,** Ag_3AsO_3, is precipitated by the addition of silver ion to neutral arsenite solution. **Iodine,** in neutral solution, is decolorized by arsenous acid, with the formation of both iodide and arsenate ions (see Arsenic, page 177*ff.*).

PRELIMINARY EXPERIMENTS

1. Add an excess of $BaCl_2$-$CaCl_2$ reagent to 1 ml. of Na_3AsO_4 solution. Treat the precipitate with dilute HCl. Repeat, using $NaAsO_2$ solution.

2. Saturate a cold solution of $NaAsO_2$, slightly acid with dilute HCl, with H_2S. Repeat, using Na_3AsO_4 solution. Treat a hot acid (HCl) solution of $AsO_4^{\equiv}$ with solid Na_2SO_3, and pass H_2S into the resulting solution.

3. Make a cold solution of Na_3AsO_4 ammoniacal, and add an excess of magnesia mixture. Repeat with a cold solution of $NaAsO_2$.

4. Dissolve a portion of the precipitate from step 3 in dilute HCl. Add equal volumes of 0.1*N* KI solution and CCl_4 and five times this volume of concentrated HCl. Shake.

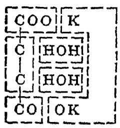
5. Dissolve another portion of the precipitate in dilute HNO_3, add a large excess of ammonium molybdate reagent, and boil.

6. To a solution of Na_3AsO_4, add $AgNO_3$ solution. Repeat with $NaAsO_2$ solution.

Tartrate, $C_4H_4O_6^{=}$

Tartrates are the salts of the organic acid, tartaric acid, $H_2C_4H_4O_6$. The latter occurs both free and as the acid potassium salt in the juice of many fruits. It is often found deposited as potassium acid tartrate, cream of tartar, $KHC_4H_4O_6$, in old wine casks. Tartrates, although organic substances, are conventionally included in the inorganic schemes of analysis. Potassium acid tartrate is used in cream of tartar baking powders. Rochelle salts, sodium potassium tartrate, $NaKC_4H_4O_6$, and tartar emetic, potassium antimonyl tartrate, $K(SbO)C_4H_4O_6$, are used in medicine.

Calcium tartrate, $CaC_4H_4O_6$, is soluble in acetic acid and in concentrated alkali hydroxides. Barium ion precipitates white **barium tartrate,** $BaC_4H_4O_6$. On treatment of tartrates with **concentrated sulfuric acid,** SO_2, CO_2, and carbon are formed, the mixture, meanwhile, evolving a characteristic "burned-sugar" odor. The decomposition may be represented as follows:



From solutions of neutral tartrates, silver ion precipitates white **silver tartrate,** $Ag_2C_4H_4O_6$, which is soluble in nitric acid and ammonium hydroxide. On warming the ammoniacal solution, black metallic silver is precipitated, which, under certain conditions, may form a **silver mirror** on the tube. Tartrates form complex ions with many of the metal cations, as aluminum and chromium. They therefore interfere with a systematic analysis and must be removed before proceeding to a complete analysis of the metals.

When a solution of tartaric acid is treated with potassium chloride solution, **potassium acid tartrate,** $KHC_4H_4O_6$, is deposited. This reaction is catalyzed by sodium acetate.

PRELIMINARY EXPERIMENTS

1. Add an excess of $BaCl_2$-$CaCl_2$ reagent to 1 ml. of $NaKC_4H_4O_6$ solution. Treat the precipitate with dilute HCl.

2. Treat some solid $NaKC_4H_4O_6$ with concentrated H_2SO_4, and warm slightly. Test the combustibility of the vapor. Smell the vapors cautiously.

3. *Silver Mirror Test.*—Clean a small test tube thoroughly with cleaning solution and distilled water. Add some $NaKC_4H_4O_6$ solution and a slight excess of $AgNO_3$ solution. Add NH_4OH dropwise until the precipitate just dissolves. Add a drop of NaOH, and warm.

4. To a solution of tartaric acid, add a drop or two of sodium acetate solution and some KCl solution.

Chromate and Dichromate, $CrO_4^{=}$, $Cr_2O_7^{=}$

Chromates are found only rarely in nature. They are usually manufactured from chromite ore, $FeCr_2O_4$, by fusion with sodium carbonate in contact with air. **Chromates** are converted to **dichromates** on treatment with acid.

With Ba^{++}, yellow **barium chromate,** $BaCrO_4$, is precipitated from solutions of both $CrO_4^{=}$ and $Cr_2O_7^{=}$. The precipitate is insoluble in acetic acid but soluble in hydrochloric and nitric acids. With Ag^{+}, brick-red **silver chromate,** Ag_2CrO_4, is precipitated that is soluble in HNO_3 and NH_4OH. Lead ion precipitates **lead chromate,** $PbCrO_4$, which is soluble in nitric acid and potassium hydroxide. When chromates are treated with hydrogen peroxide and sulfuric acid, they are oxidized to blue so-called **perchromic acid** (CrO_5) which is diperoxy chromium oxide, $CrO(O_2)_2$, in which chromium has a valence of 6. This compound is very soluble in ether. **Hydrogen sulfide** or **alcohol** reduces chromates to the **chromic** state:

$$16H^{+} \qquad\qquad 3S^{=} \quad \cdot 2Cr^{+++} + 3S + 8H_2O$$

These reactions may be used to remove chromates. With **diphenyl carbazide,** acid solutions of $CrO_4^{=}$ or $Cr_2O_7^{=}$ yield a violet color.

Preliminary Experiments

1. Add an excess of $BaCl_2$-$CaCl_2$ reagent to 1 ml. of K_2CrO_4 solution. Treat the precipitate with dilute HCl.

2. Treat some K_2CrO_4 solution, acidified with dilute HCl, with ethyl alcohol, and boil. Pass H_2S into an acidified (HCl) K_2CrO_4 solution.

3. Treat K_2CrO_4 solution with $AgNO_3$ solution. Treat portions of the precipitate with dilute HNO_3 and dilute NH_4OH.

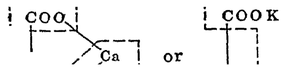
4. Acidify some K_2CrO_4 solution with dilute H_2SO_4, add 1 ml. of ether, then some H_2O_2, and shake well (**CAUTION**).

5. To 2 drops of K_2CrO_4 solution, acidified with H_2SO_4, add an equal volume of diphenyl carbazide solution.

OXALATE, $C_2O_4^{=}$

Oxalic acid is an organic acid that is found in many plants in the form of the calcium and acid potassium salts. It is prepared commercially by heating sawdust and sodium hydroxide. Oxalic acid, although organic, is conventionally included in the inorganic scheme of analysis. It is used commercially as a cleaning agent for removing stains, especially rust spots. Oxalic acid, taken internally, is a violent poison.

Barium oxalate, BaC_2O_4, is soluble in acetic acid. **Calcium oxalate,** CaC_2O_4, is, however, insoluble in acetic acid but is readily soluble in hydrochloric or nitric acid. Oxalates will decolorize an acid solution of **potassium permanganate,** giving CO_2 and manganous ion, Mn^{++}. With **concentrated sulfuric acid,** oxalates yield equal volumes of CO_2 and CO. The decomposition may be represented as follows:



Silver ion precipitates white **silver oxalate,** $Ag_2C_2O_4$, which is soluble in nitric acid and ammonium hydroxide. When a precipitate of **manganous manganic hydroxide,** obtained by the treatment of manganous sulfate with sodium hydroxide, is treated with a solution of an oxalate, slightly acid with sulfuric acid, a red coloration, probably due to the trioxalato manganite ion, $[Mn(C_2O_4)_3]^{\equiv}$, is obtained.

PRELIMINARY EXPERIMENTS

1. Add an excess of $BaCl_2$-$CaCl_2$ reagent to 1 ml. of solution. Treat portions of the precipitate with dilute HCl.
2. Add a slight excess of $AgNO_3$ solution to some solution. Treat portions of the precipitate with dilute HNO_3 and dilute NH_4OH.
3. Treat an acidified (H_2SO_4) solution of $(NH_4)_2C_2O_4$ with dilute $KMnO_4$ solution.
4. Warm gently a solution of a small crystal of manganous sulfate in a few drops of water, to which a drop of NaOH has been added. Cool, and add dropwise an acidified (H_2SO_4) solution of (Interferences: reducing agents.)

BORATE, $BO_3^{\equiv}$ (BO_2^-, $B_4O_7^=$)

Borates are found in nature chiefly as borax, sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$. There are several boric acids, orthoboric acid, H_3BO_3, metaboric acid, HBO_2, and pyroboric acid or tetraboric acid, $H_2B_4O_7$. The latter is known only in the form of its salts. Borax is used as a detergent (cleaning agent), as a flux, and in the making of glass. Orthoboric acid is commonly used as an eyewash.

The salts of orthoboric acid are unknown in the pure state. The borates, therefore, are generally salts of meta- or pyroboric acid.

Barium ion precipitates white **barium metaborate,** $Ba(BO_2)_2$, from solutions of borax. This is explained by the fact that a solution of borax ionizes as follows:

$$Na_2B_4O_7 + 3H_2O \rightleftharpoons 2Na^+ + 2BO_2^- + 2H_3BO_3$$

Upon further dilution, more unionized orthoboric acid is formed, and the solution becomes more alkaline.

$$BO_2^- + 2H_2O \rightleftharpoons OH^- + H_3BO_3$$

Calcium metaborate is soluble in acetic acid. Moderately concentrated solutions of borax give, with Ag^+, a precipitate of white **silver metaborate,** $AgBO_2$, which readily changes to brown silver oxide, Ag_2O, on dilution.

On treatment with concentrated sulfuric acid and alcohols, such as ethyl or methyl alcohol, volatile **triethyl** or **trimethyl orthoborate,** $(C_2H_5)_3BO_3$ or $(CH_3)_3BO_3$, is formed; this burns with a green flame. Boric acid turns turmeric paper reddish brown, which color is stable to dilute hydrochloric or sulfuric acid and which turns bluish black if moistened with sodium hydroxide solution. Oxidizing agents interfere with this test.

PRELIMINARY EXPERIMENTS

1. Add an excess of $BaCl_2$-$CaCl_2$ reagent to 1 ml. of $Na_2B_4O_7$ solution. Treat the precipitate with dilute HCl.
2. Treat a concentrated solution of $Na_2B_4O_7$ with $AgNO_3$ solution. Dilute and warm.
3. To a small amount of solid $Na_2B_4O_7$ in a crucible, add concentrated H_2SO_4 and some ethyl alcohol. Ignite the vapors.
4. Acidify a solution of $Na_2B_4O_7$ with dilute HCl, and place a drop of this solution on turmeric paper. Dry the paper, and then touch with a drop of dilute NaOH. (Interferences: chromate, nitrate, chlorate, iodide.)

SILICATE, $SiO_4^{\equiv}$

Silicates comprise a large part of the earth's crust. They are essential constituents of most rocks and many minerals. Pure silica has the formula SiO_2. The formulae of the silicates vary, silicon assuming a variety of valence numbers. This might be expected since silicon falls in the same group in the periodic table as carbon. In the various minerals, the silicates are present in the form of giant molecules. There are three forms of giant molecules, the thread form, typified by asbestos, which has a cross section of one molecule and is x molecules in length; the plate form, typified by the micas, which is one molecule thick and of undetermined length in the other two dimensions; and the massive form, typified by olivine, beryl, etc., which extends endlessly in three directions.

Natural silicates are used as building materials. Many manufactured silicates are also employed in this way, as Portland cement. Another important silicate used in industry is silica, SiO_2, which is used in the manufacture of fused silica laboratory apparatus and mercury-vapor tubes, and in the manufacture of glass. Glass is a supercooled liquid that consists essentially of a mixture of silicates of the alkali metals and metals of Group II and III of the periodic table. Ordinary soft glass contains the silicates of sodium and calcium; glass used in crystal ware contains large amounts of lead silicate. Hard Bohemian glass contains potassium, replacing a large amount of sodium. Pyrex glass has as an essential constituent large amounts of boron. Other types of glass contain other elements.

Soluble silicates, like **sodium silicate,** are used in industry as detergents (cleaning agents). Sodium silicate is usually sold as a water solution. **Soluble silicates,** when heated with concentrated hydrochloric acid, precipitate silica, SiO_2. Most silicates, when fused in a **phosphate bead,** leave a silica skeleton in the clear bead.

ANALYSIS OF GROUP II ANIONS

1. Group Reagent.—Dissolve a portion of solid unknown in water, and make alkaline with NH_4OH. Add some $BaCl_2$-$CaCl_2$ solution, stir, and allow to stand for a little while. If the precipitate formed is yellow, the presence of chromate is indicated. Treat the precipitate with dilute HCl. All the Group II anions are soluble, with the exception of $BaSO_4$ and CaF_2, the slimy precipitate of the latter being slightly soluble. If a precipitate remains, test it for sulfate and fluoride, as in steps 5 and 8, and test the filtrate for chromate, as in step 4.

2. Oxidizing Acids.—Dissolve a portion of the unknown in water, and add half its volume of concentrated HCl and then two-thirds the volume of a saturated solution of $MnCl_2$ in concentrated HCl. A brown or black color indicates the presence of chromate.

3. Reducing Acids.—Acidify a portion of the aqueous solution of the unknown with dilute H_2SO_4, and treat with a few drops of dilute $KMnO_4$ solution. Disappearance of the color indicates the presence of one or more of the following anions: AsO_2^-, $C_2O_4^=$, or $C_4H_4O_6^=$. If the color does not disappear in the cold, warm gently.

4. Chromate.—If the original precipitate obtained in step 1 is yellow, make the filtrate from step 1 ammoniacal, and dissolve the precipitate formed in dilute H_2SO_4. Add some H_2O_2 and ether, and shake.

Blue color in ether layer confirms **chromate.**

5. Sulfate.—Fuse some of the precipitate from step 1 with Na_2CO_3 and powdered charcoal with a blowpipe flame on the charcoal block. Place the fused mass on a clean silver coin, and add a drop of water.

Black stain proves **sulfate.**

6. Tartrate.—Treat a portion of the solid unknown with concentrated H_2SO_4; warm slightly.

Blackening of the solid, burned odor, and evolution of SO_2 indicate **tartrate.**

In the presence of reducing agents, it is often necessary to separate tartrate before testing. This may be accomplished as follows: Prepare a concentrated solution of the unknown, acidify with dilute acetic acid, add a drop of $NaC_2H_3O_2$ and some $KC_2H_3O_2$ solution, and let stand. A precipitate of $KHC_4H_4O_6$ is obtained, which is tested for the anion by the silver-mirror test.

7. Oxalate.—Dissolve a portion of the original unknown in water acidified with acetic acid, and add $CaCl_2$ solution. The precipitate may be either CaF_2 or CaC_2O_4. Filter, and reserve the filtrate for step 9. Dissolve a portion of the precipitate in dilute H_2SO_4, add $KMnO_4$ solution, and warm if necessary.

Bleaching indicates **oxalate.**

8. Fluoride.—Place the remainder of the precipitate from step 7 in a clean lead dish, and add sufficient concentrated H_2SO_4 to make a paste. Cover immediately with a soft-glass plate (not a watch glass) that has been coated with paraffin, through which a characteristic

symbol has been scratched. Allow to stand for a number of hours, preferably overnight.

Etching of the glass proves **fluoride.**

NOTE: The use of soft-glass plate like a piece of window glass is recommended for this test. This type of glass reacts more readily with HF than a Pyrex plate or watch glass.

9. Borate.—Evaporate the filtrate from step 7 just to dryness. Cool, add concentrated H_2SO_4 and ethyl alcohol, and ignite the vapors.

Green flame proves **borate.**

10. Arsenate.—Make a cold solution of a portion of the original unknown (do not heat) ammoniacal, and treat with a slight excess of magnesia mixture. A precipitate indicates the presence of arsenate or phosphate or both. Filter, and reserve the filtrate for step 12. Dissolve a small portion of the precipitate in dilute HCl. Add equal volumes of $0.1N$ KI solution and CCl_4 and five times this volume of concentrated HCl. Shake.

Violet coloration in CCl_4 layer indicates **arsenate.**

If arsenate is indicated, dissolve the remainder of the precipitate in dilute HCl, and add solid Na_2SO_3 in small portions until all the arsenate has been reduced. Saturate the solution with H_2S.

Yellow precipitate of As_2S_3 proves **arsenate.**

11. Phosphate.—Filter the precipitate from step 10, and boil the filtrate to expel excess H_2S. Cool, add an excess of dilute HNO_3 and $(NH_4)_2MoO_4$ reagent, and heat.

Yellow precipitate proves **phosphate.**

12. Arsenite.—Acidify the filtrate from step 10 with dilute HCl, and saturate with H_2S.

Immediate precipitation of As_2S_3 proves **arsenite.**

GROUP III ANIONS

FERROCYANIDE, $Fe(CN)_6^{\equiv}$

The **free acid,** $H_4Fe(CN)_6$, is a white crystalline solid that is readily soluble in water. It is prepared by acidifying a concentrated aqueous solution of potassium ferrocyanide, $K_4Fe(CN)_6$. Neither the acid nor its salts are found free in nature. The anion is a good example of a

stable complex. Both the acid and its solution are oxidized in air, depositing a blue compound that is probably ferri-ferrocyanide.

Only the ferrocyanides of the **alkali** and **alkaline earth metals** are water soluble; all the others are insoluble. The most common salt is potassium ferrocyanide. It may be obtained as a by-product in the coking of coal. Soluble ferrocyanides are yellow when hydrated, white when in the anhydrous state. **Ferrocyanides** are mild reductants and are readily oxidized in acid solution to **ferricyanide,** $Fe(CN)_6^{\equiv}$. A number of reagents may be used to bring about this reaction: H_2O_2, Br_2, MnO_4^-, $Cr_2O_7^=$, HNO_3, and many others.

Silver nitrate gives a white precipitate of **silver ferrocyanide,** $Ag_4Fe(CN)_6$, when added to a soluble ferrocyanide. The precipitate is insoluble in both dilute nitric acid and ammonium hydroxide. With concentrated nitric acid, it is converted to the orange **silver ferricyanide.** Ferrocyanides yield, with cobalt nitrate, a green precipitate of **cobalt ferrocyanide,** $Co_2Fe(CN)_6$, which is insoluble in dilute acetic and hydrochloric acids. With **ferric ion,** ferrocyanide ion yields a blue precipitate, $Fe_4[Fe(CN)_6]_3$, the well-known **Prussian Blue. Ferrous ion** yields a white precipitate that gradually turns blue on exposure to air, through oxidation to Prussian Blue. In the presence of acetic acid, ferrocyanide ion gives a brown precipitate of **cupric ferrocyanide,** $Cu_2Fe(CN)_6$, when treated with a solution of $CuSO_4$. Lead salts produce white **lead ferrocyanide,** $Pb_2Fe(CN)_6$, which is insoluble in dilute nitric acid.

Ferrocyanides, when boiled with mercuric oxide, are transposed. Prussian Blue, for example, treated with a suspension of yellow **mercuric oxide,** HgO, is decomposed, yielding ferrous hydroxide, $Fe(OH)_2$, ferric hydroxide, $Fe(OH)_3$, and mercuric cyanide, $Hg(CN)_2$.

PRELIMINARY EXPERIMENTS

[*Use only freshly prepared $K_4Fe(CN)_6$ solution*]

1. Treat 0.5 ml. of $K_4Fe(CN)_6$ solution with a slight excess of $AgNO_3$ solution. Treat the precipitate with concentrated HNO_3.
2. Add several drops each of dilute $HC_2H_3O_2$ and $2N$ $Co(NO_3)_2$ to a portion of $Fe(CN)_6^{\equiv}$ solution.
3. Acidify a portion of $K_4Fe(CN)_6$ solution with dilute HCl, and add a few drops of $FeCl_3$ solution. Treat the blue precipitate with a suspension of yellow HgO.
4. Treat some of the ferrocyanide solution, prepared from a clean crystal, with ferrous ammonium sulfate solution. Note the progressive color changes of the precipitate on exposure to air.

5. Acidify a few drops of $K_4Fe(CN)_6$ solution with dilute acetic acid, and add some $CuSO_4$ solution.

6. Add $Pb(NO_3)_2$ solution to the ferrocyanide solution. Treat the precipitate with dilute HNO_3.

FERRICYANIDE, $Fe(CN)_6^{\equiv}$

Anhydrous **ferricyanic acid,** $H_3Fe(CN)_6$, is a brown crystalline substance that is readily soluble in water, giving a strongly acid solution. The corresponding salts, the **ferricyanides,** are very stable and are generally obtained by oxidation of the corresponding ferrocyanides.

The ferricyanides of the **alkali, alkaline earth** metals, and **ferric** ion are water-soluble; all the others are insoluble. Solutions of ferricyanides are reddish in color, although the ferric salt gives a brownish solution. The reaction of ferricyanide ion with various cations produces precipitates of varied and pronounced colors. Silver ion forms orange-red **silver ferricyanide,** $Ag_3Fe(CN)_6$, which is insoluble in dilute nitric acid but is soluble in ammonium hydroxide. With ferrous ion, a deep blue precipitate of **Turnbull's Blue,** $Fe_3[Fe(CN)_6]_2$, is obtained. When this precipitate is treated with KOH, both ferrous and ferric hydroxides are precipitated, and the solution contains ferrocyanide ion.

A green precipitate of **cupric ferricyanide,** $Cu_3[Fe(CN)_6]_2$, is obtained when Cu^{++} is added to soluble ferricyanides. Ferric salts produce no precipitate but yield only a brown solution of **ferri-ferricyanide,** $Fe[Fe(CN)_6]$. In contrast to ferrocyanide, no precipitate is obtained when ferricyanide solutions are treated with **lead salts.** In the presence of acetic acid, ferricyanide yields, with Co^{++}, a reddish precipitate of **cobalt ferricyanide,** $Co_3[Fe(CN)_6]_2$. In acid solution, ferricyanide is reduced to ferrocyanide by **potassium iodide,** KI, which is in turn oxidized to free iodine. This reaction forms the basis for the quantitative estimation of the anion. As an oxidizing acid, also, ferricyanide converts a hydrochloric acid solution of $MnCl_2$ to the dark brown Mn^{++++} ion.

PRELIMINARY EXPERIMENTS

[*Use only freshly prepared $K_3Fe(CN)_6$ solution*]

1. Add a slight excess of $AgNO_3$ solution to $K_3Fe(CN)_6$ solution. Treat separate portions of the precipitate with dilute HNO_3 and dilute NH_4OH.

2. Add a portion of ferricyanide solution to a saturated solution of $MnCl_2$ in concentrated HCl.

3. Acidify a portion of $Fe(CN)_6^{\equiv}$ with dilute HCl, and add a few drops of a freshly prepared solution of ferrous ammonium sulfate. Boil some of the precipitate with KOH solution. Filter and acidify the filtrate and treat with $FeCl_3$ solution.

4. Add a few drops of $CuSO_4$ solution to an acidified ($HC_2H_3O_2$) solution of potassium ferricyanide.

5. Treat ferricyanide solution with $Pb(NO_3)_2$ solution.

6. To an acidified (HCl) solution of ferricyanide, add an equal volume of KI solution.

7. Add several drops of dilute acetic acid and $2N$ $Co(NO_3)_2$ solution to the ferricyanide solution.

Thiocyanate, CNS^-

Thiocyanic acid, HCNS, is an oily liquid readily soluble in water, giving an aqueous solution whose strength is about equal to that of hydrochloric acid. It is not very stable, however, and decomposes with the liberation of HCN. The salts are much more stable. **Alkali thiocyanates** may readily be prepared by heating the corresponding cyanide with ammonium polysulfide (see Cyanide, page 230).

Practically all the thiocyanates are water-soluble, the only exceptions being the **silver, mercury,** and **copper salts.** However, even these are soluble in excess of CNS^- with the formation of complex ions. Silver ion reacts with CNS^- to form a white, curdy precipitate of **silver thiocyanate,** AgCNS, which is soluble in ammonium hydroxide but is insoluble in dilute nitric acid. The precipitate may be transposed by boiling with 5% NaCl solution, yielding silver chloride and a solution of sodium thiocyanate, NaCNS. This fact is utilized in the separation of AgCNS from AgI. Ignition of silver thiocyanate results in decomposition with the formation of black **silver sulfide,** which reaction may be used to separate and distinguish the anion from the halides. With ferric ion, a red complex, $Fe(CNS)^{++}$, is obtained that is readily soluble in ether. Mercuric nitrate, with CNS^-, yields a white precipitate of **mercuric thiocyanate,** $Hg(CNS)_2$, which is soluble in an excess of KCNS with the formation of the complex ion, $[Hg(CNS)_3]^-$. The potassium salt of the latter, when heated, expands into peculiar shapes (Pharaoh's serpents).

Cupric ion produces an emerald-green solution with thiocyanate ions; with an excess of the reagent a black precipitate of **cupric thiocyanate,** $Cu(CNS)_2$, is produced. However, in the presence of sulfurous acid, a white precipitate of **cuprous thiocyanate,** $Cu_2(CNS)_2$, is obtained. Thiocyanate ion catalyzes the reaction between **sodium**

azide and **iodine** with the evolution of nitrogen gas. Sulfide and thiosulfate ions also catalyze this reaction.

PRELIMINARY EXPERIMENTS

1. Add a slight excess of $AgNO_3$ solution to about 0.5 ml. of NH_4CNS solution. Boil a portion of the precipitate with 5% NaCl solution for a few minutes. Filter, and treat the filtrate with $FeCl_3$ solution. Treat a portion of the precipitate with dilute NH_4OH.

2. Treat NH_4CNS solution with dilute $FeCl_3$. Shake a portion of the solution with some ether (**CAUTION**). To the remainder add $Hg(NO_3)_2$ solution.

3. To some of the CNS^- solution add lead nitrate solution.

4. Add NH_4CNS solution dropwise to a little $CuSO_4$. Divide the solution into two portions. Add an excess of CNS^- to one portion. To the other, add a solution of H_2SO_3, prepared by acidifying a solution of Na_2SO_3.

5. Mix 1 drop of NH_4CNS solution with an equal volume of NaN_3-I_2 reagent on a spot plate.

Chloride, Cl^-

Hydrochloric acid is an aqueous solution of the extremely soluble gas, hydrogen chloride. The concentrated solution contains from 36 to 37% HCl. Dilute HCl is a very strong acid, being highly ionized. The salts of the acid are very common and abundant, particularly the sodium and potassium salts.

Strong oxidizing agents, like PbO_2, $KMnO_4$, etc., convert the acid into free **chlorine.** Concentrated **nitric acid** liberates some **nitrosyl chloride,** NOCl, as well as chlorine. When these acids are mixed in the ratio of 1 part HNO_3:3 parts HCl by volume, the resulting solution is called aqua regia and serves as an excellent solvent for gold and the platinum metals.

Most of the **metallic chlorides** are soluble in water, the exceptions being the salts of **silver, lead, mercurous mercury, cuprous copper,** and the **basic chlorides of antimony** and **bismuth.** The sodium salt, NaCl, is common table salt. A white, curdy precipitate of **silver chloride,** AgCl, is obtained when silver nitrate is added to a soluble chloride. The precipitate is soluble in ammonium hydroxide, sodium thiosulfate, and potassium cyanide (see reactions of Silver. Cation Group I). Silver chloride may be **transposed** by reduction with metallic zinc and dilute sulfuric acid, **metallic silver** being precipitated and the **chloride ion** passing into solution.

Anhydrous chlorides, when treated with potassium dichromate, $K_2Cr_2O_7$, and concentrated sulfuric acid, are converted to the brownish red gas **chromyl chloride,** CrO_2Cl_2. When the gas is absorbed in sodium hydroxide solution, sodium chromate is formed, which is tested for in the usual manner. This test confirms the presence of chlorides.

PRELIMINARY EXPERIMENTS

1. To 1 ml. of NaCl solution add a slight excess of $AgNO_3$ solution. Treat a portion of the white precipitate with an excess of dilute NH_4OH. Acidify the resulting solution with dilute HNO_3. Boil the remainder of the precipitate with dilute H_2SO_4 and metallic Zn. Filter, and test the filtrate for Cl^-.
2. Add a few drops of concentrated H_2SO_4 to a few crystals of solid NaCl. Hold a glass rod, wet with dilute NH_4OH, over the mouth of the tube.
3. Mix a small amount of solid NaCl with twice its weight of finely powdered $K_2Cr_2O_7$, and place the mixture in a micro gas generator. (*The apparatus must be perfectly dry.*) Add several drops of concentrated H_2SO_4, and heat on a sand bath for several minutes. Collect the gas evolved in dilute NaOH. Make the solution acid with dilute H_2SO_4, add several drops each of ether and H_2O_2, and shake.

Bromide, Br^-

Hydrobromic acid is formed by solution of the gas, hydrogen bromide, in water. It is a strong acid but is not so stable as hydrochloric acid. On exposure to light, it is oxidized with the evolution of free bromine, which imparts a yellow color to the solution. In general, hydrobromic acid is more easily oxidized than hydrochloric acid.

The metallic bromides resemble the chlorides, both in solubility and chemical behavior. Sodium and potassium bromides are used medicinally as sedatives. Only the **silver, mercurous, cuprous,** and **lead bromides** are insoluble in water. Silver nitrate precipitates, from soluble bromides, curdy yellow-white **silver bromide,** AgBr, insoluble in nitric acid, less soluble in ammonium hydroxide than AgCl, but readily soluble in potassium cyanide and sodium thiosulfate, forming complexes of the same type as silver chloride. The precipitate may be **reduced** with zinc and sulfuric acid, or it may be **transposed** by boiling with 5% NaCl solution, yielding, in either case, a solution of the bromide ion. Conversion takes place, with NaCl, to the extent of about 20%.

Oxidation of bromides and hydrobromic acid with oxidizing agents, like $KMnO_4$, results in the evolution of free bromine that is soluble in and imparts a brown to red color to carbon tetrachloride, CCl_4. A sensitive test for bromides involves the action of free bromine on the organic dye **fluorescein.** In this reaction, the organic compound is converted to the red dye, **eosin.** The latter is the familiar coloring matter of red ink and indelible lipsticks.

PRELIMINARY EXPERIMENTS

1. Add a slight excess of $AgNO_3$ solution to KBr solution. Treat a portion of the precipitate with dilute NH_4OH. Boil another portion of the precipitate with dilute H_2SO_4 and granular Zn, filter, and test the filtrate for Br^-. Boil the remainder of the AgBr with 5% NaCl solution for several minutes. Filter, and test the filtrate for Br^-.

2. Treat some of the KBr solution with several drops of an acidified (H_2SO_4) solution of $KMnO_4$. Add some CCl_4 to the solution, and shake the tube.

3. Add several drops of concentrated H_2SO_4 to some solid KBr. Hold a strip of paper impregnated with fluorescein in the mouth of the tube.

IODIDE, I^-

Hydrogen iodide, HI, is a colorless gas, with an irritating odor, which is extremely soluble in water, forming hydriodic acid. It is a strong acid and is highly ionized but is less stable than either hydrobromic or hydrochloric acid. It is oxidized in air, liberating free iodine, which imparts a brown color to the solution. Hydriodic acid is easily oxidized by chemical agents even in the cold.

The metallic iodides of **lead, cuprous** and **mercury** ions are more insoluble in water than the corresponding chlorides and bromides. Sodium and potassium iodides are used medicinally in the treatment of goiter. This disease is caused by lack of the hormone thyroxin, an organic iodo compound found in the thyroid gland.

Silver nitrate forms a yellow precipitate of **silver iodide,** AgI, which is insoluble in nitric acid and is only very slightly soluble in ammonium hydroxide. It is, however, readily soluble in potassium cyanide and sodium thiosulfate solutions. Silver iodide may be **reduced** with zinc and sulfuric acid, but it is **not transposed** by boiling NaCl solution. Lead salts precipitate yellow **lead iodide,** PbI_2, which is sparingly soluble, even in hot water. **Hydrogen peroxide** oxidizes iodide solutions to free iodine, which imparts a violet color to carbon tetrachloride, in which it is soluble. Other oxidizing agents bring about the

same reaction. **Concentrated sulfuric acid,** acting on iodides, evolves free iodine. **Nitrous acid** also liberates free iodine, which turns starch solution a blue color.

PRELIMINARY EXPERIMENTS

1. Add a slight excess of $AgNO_3$ solution to KI solution. Test the solubility of the precipitate in NH_4OH. Boil the remainder of the precipitate with dilute H_2SO_4 and Zn, filter, and test the filtrate for I^-.
2. Treat a portion of the I^- solution, to which some CCl_4 has been added, with several drops of H_2O_2. Shake the tube and contents.
3. Add concentrated H_2SO_4 to a few crystals of KI, and warm gently.
4. To a few drops of $Pb(NO_3)_2$ solution, add KI until precipitation is complete. (Interference: ferrocyanide.)
5. Place a drop of acidified I^- solution (HCl) on a spot plate, and add equal volumes of starch solution and KNO_2 solution.

ANALYSIS OF GROUP III ANIONS

1. Group Reagent.—Dissolve a portion of the unknown in water, and make the solution distinctly acid with dilute HNO_3. Add $AgNO_3$ solution dropwise until no further precipitation occurs. The presence of certain anions is indicated by the color of the precipitate. Ferrocyanide, thiocyanate, and chloride give white precipitates; bromide is yellow-white; iodide, yellow; and ferricyanide, orange.

NOTE: In the event that only Cl^-, Br^-, and I^- are present, it should be noted that AgI precipitates first, then AgBr, and finally AgCl.

2. Oxidizing Acids.—Treat a portion of the unknown solution with half its volume of concentrated HCl, and then add two-thirds the volume of a saturated solution of $MnCl_2$ in concentrated HCl. The appearance of a brown to black coloration indicates the presence of ferricyanide.

3. Reducing Acids.—Dissolve a portion of the unknown in water, and acidify the solution with dilute H_2SO_4. Treat the solution with a few drops of $0.1N$ $KMnO_4$ solution. Bleaching of the solution indicates the presence of one or more of the following anions: $Fe(CN)_6^{\equiv}$, Br^-, and I^-.

4. Action of Concentrated H_2SO_4.—Treat a small portion of the well-mixed solid unknown with a few drops of concentrated H_2SO_4, and warm gently. The evolution of brown fumes indicates Br^-; violet fumes indicate I^-.

5. Test for Ferrocyanide, Ferricyanide, and Thiocyanate in the Presence of Each Other.—On a piece of good filter paper, place a drop of $Pb(NO_3)_2$ solution, and allow it to absorb completely. Add a drop of the unknown solution to the center of the wet spot. When this has absorbed completely, add another drop of $Pb(NO_3)_2$ solution. After complete absorption of this last drop, spread the spot by adding, singly, 2 to 3 drops of water. The spot should now be about 7 cm. in diameter. Ferrocyanide is now precipitated at the center as the lead salt. Ferricyanide and thiocyanate have diffused to the periphery of the spot. With a capillary dropper, draw a thin line of a solution of ferrous ammonium sulfate across the spot.

A deep blue where the line crosses the periphery of the spot proves **ferricyanide.**

With another capillary dropper, draw a line across the spot, at right angles to the first line, with $FeCl_3$ solution.

A red coloration, at the periphery, proves **thiocyanate.**
A blue spot in the center proves **ferrocyanide.**

NOTE: There may appear occasionally a light blue coloration at the center, where the ferrous sulfate line crosses it. This is caused either by slight contamination of the ferrous salt with ferric ion, or by air oxidation of the white ferro-ferrocyanide. For this reason, the ferrous salt solution should always be freshly prepared from a *clean green crystal* of ferrous ammonium sulfate.

6. Cobalt Nitrate Separation.—If ferro- and ferricyanides are absent, proceed directly as in step 7. If these anions are present, proceed as follows: Acidify a portion of the unknown solution with dilute acetic acid. Add an excess of $2N$ $Co(NO_3)_2$ to the solution, with vigorous stirring. Treat with approximately 0.1 g. of washed asbestos, boil the solution for about 12 min., and filter. Wash the precipitate twice with hot water, adding the washings to the filtrate, and discard the precipitate.

7. Make the filtrate from step 6 slightly alkaline with dilute NaOH, and then make it distinctly acid with concentrated HNO_3. (If ferro- and ferricyanides are absent, the original unknown may be acidified directly.) Add a slight excess of $AgNO_3$ solution, with vigorous stirring. Filter and wash the precipitate, and discard the filtrate and washings.

8. Bromide.—Treat a portion of the precipitate from step 7 with 5% NaCl solution, and boil for about 5 min. Filter, and discard the

precipitate. The filtrate contains bromide, or thiocyanate, and chloride. Add some CCl_4 and H_2O_2 to the solution, and shake.

Red-brown color in CCl_4 (lower layer) proves **bromide.**

9. Separation of Chloride and Iodide.—If CNS^- is present, ignite the remainder of the precipitate from step 7 until it turns black and the burning of sulfur ceases, and proceed as below. If CNS^- is absent, proceed directly with the following step. Treat the residue with dilute H_2SO_4 and granular Zn, and boil for 3 to 5 min. Filter, wash the precipitate with hot water, and discard the precipitate.

10. Iodide.—Treat a portion of the filtrate from step 9 with H_2O_2 and CCl_4, and shake for several seconds.

Violet coloration in CCl_4 layer proves **iodide.**

11. Chloride.—If iodide and bromide are present, they are removed by boiling the remainder of the solution from step 9 with HNO_3 until no more fumes of Br_2 or I_2 are evolved. Treat the solution with a slight excess of $AgNO_3$

White precipitate proves **chloride.**

GROUP IV ANIONS

NITRATE, NO_3^-

Nitrates are found in quantity in nature, as sodium nitrate (Chile saltpeter), in the rainless deserts of Chile and in other parts of the world. They are widely distributed in the soil as ammonium nitrate, which is essential to the growth of plants. Nitric acid, HNO_3, is manufactured by the oxidation of ammonia formed by combination of nitrogen and hydrogen under high pressure and medium temperature (Haber process). Nitrates are used in fertilizers, gunpowder, and in many industries.

Nitrates, in general, are soluble in water, although a few react with water to give insoluble oxynitrates (hydroxynitrates). Nitric acid is a strong oxidizing agent. With metals, it does not yield hydrogen (with some exceptions) but gives, instead, water and some of the lower oxides of nitrogen or ammonia, depending upon the conditions and the metal used. Concentrated nitric acid renders many metals passive (incapable of reacting). A notable example of this phenomenon is aluminum, which is rendered so passive that nitric acid is now shipped in drums made of this metal. The concentrated acid forms aqua regia with concentrated hydrochloric acid. This is a mixture of nitrosyl chloride,

NOCl, and free chlorine. **Concentrated sulfuric acid** reacts with nitric acid with the liberation of nitrous fumes; dilute sulfuric acid does not bring about this reaction, in contradistinction to nitrous acid (*q.v.*).

Ferrous ion, acted upon by nitric acid, is oxidized to ferric ion, with the evolution of nitric oxide, NO. The oxide combines with more of the ferrous ion to form a brown compound, $FeSO_4 \cdot NO$. This is the basis of the so-called **brown-ring** test for nitrates. **Aluminum, or zinc, and sodium hydroxide** will, on heating, reduce nitrates to ammonium ion. **Brucine sulfate,** in concentrated sulfuric acid, added to a solution of nitrate in concentrated sulfuric acid gives a deep red coloration which fades through a range of colors to give, finally, a greenish yellow color.

PRELIMINARY EXPERIMENTS

1. Treat a portion of $NaNO_3$ with concentrated H_2SO_4. Repeat the test with dilute H_2SO_4.
2. Add NaOH solution to a solution of NO_3^-, and boil. Smell the vapors, and hold a piece of moist red litmus paper over the mouth of the tube. Cool the tube, add some aluminum dust, and boil again. Smell the vapors, and hold a piece of moist red litmus paper over the mouth.
3. Place a tiny crystal of ferrous sulfate or of ferrous ammonium sulfate in a depression on the spot plate. Cover with a drop of $NaNO_3$ solution, and add a drop of concentrated H_2SO_4 down the side of the depression.
4. Mix some $NaNO_3$ solution with three times its volume of concentrated H_2SO_4, and treat with a few drops of a solution of brucine in concentrated H_2SO_4.

Chlorate, ClO_3^-

Free chloric acid, $HClO_3$, is quite unstable, decomposing into perchloric acid, $HClO_4$, and liberating chlorine and oxygen. It is a very strong oxidizing agent. The most common salt is the potassium salt, $KClO_3$. This compound is used in the manufacture of matches, fireworks, and some explosives.

Although all chlorates are soluble in water, some are hydrolyzed. **Potassium chlorate** is the least soluble of the stable chlorates. **Dilute sulfuric acid,** when added to a chlorate, liberates free **chloric acid,** which decomposes, yielding chlorine, oxygen, and perchloric acid. This mixture will turn starch-KI paper blue. **Concentrated sulfuric acid** reacts with chlorates to form perchloric acid and yellowish green

chlorine dioxide, ClO_2, which is violently explosive, especially on heating. Chlorine dioxide has a peculiar sweetish odor that is quite distinctive.

Chlorates are reduced by **aluminum, or zinc powder and sodium hydroxide** to chlorides. Chlorates may also be reduced in acid solution. If a drop of an aqueous **aniline sulfate** solution is added to some sulfuric acid in which a crystal of a chlorate has been placed, a deep blue color is obtained. This test is not given by nitrate.

PRELIMINARY EXPERIMENTS

1. To a drop of dilute H_2SO_4, on a spot plate, add a tiny crystal of $KClO_3$. Immerse a strip of starch-KI paper in the liquid. Repeat the test, using concentrated H_2SO_4.
2. Make a solution of $KClO_3$ strongly alkaline with NaOH, add some Al dust, and boil. Filter off the Al dust, acidify the solution with dilute HNO_3, and add an excess of $AgNO_3$ solution.
3. (*Optional*) Add a small crystal of $KClO_3$ to several drops of concentrated H_2SO_4 on a spot plate, and add a few drops of an aqueous solution of aniline sulfate.

ACETATE, $C_2H_3O_2^-$

Acetic acid, $HC_2H_3O_2$, an organic acid, occurs naturally in many plants, both free and as the potassium or calcium salt. It is obtained commercially by the dry distillation of wood or by the oxidation of ethyl alcohol. Vinegar is a dilute solution of acetic acid obtained by the oxidation of the alcohol in various fermented liquors, like wine or cider. Acetic acid itself has a very choking odor reminiscent of vinegar. The sodium and lead salts are the most important commercially used acetates.

Most of the acetates are soluble in water, although the silver salt is only sparingly soluble. **Dilute sulfuric acid** liberates acetic acid from its salts, and since the acid is quite volatile, its odor may be readily recognized, particularly if the solution is warmed. If ethyl alcohol is added to acetic acid or an acetate, concentrated sulfuric acid added, and the solution warmed, **ethyl acetate,** which has a pleasant fruity odor, is evolved. Ferric chloride, added to neutral acetate solutions in the cold, forms dark brown **ferric acetate,** $Fe(C_2H_3O_2)_3$, which, on dilution and boiling, precipitates the dark red to brown **basic ferric acetate,** $Fe(OH)_2(C_2H_3O_2)$. Acetate ion, with **iodine, ammonium hydroxide and lanthanum nitrate,** yields a dark blue precipitate that is probably due to the formation of a complex adsorption compound.

When acetates are heated strongly, **acetone,** $(CH_3)_2CO$, is evolved. When the alkali metal salts are used, the carbonate is left behind; with the alkaline earth salts, the oxide remains.

PRELIMINARY EXPERIMENTS

1. Add some dilute H_2SO_4 to an acetate, warm, and smell the vapors.
2. To several drops of an acetate solution, acidified with concentrate H_2SO_4, add several drops of ethyl alcohol. Warm the solution, and smell the vapors. Run a blank in conjunction with this test.
3. To a neutral solution of $NaC_2H_3O_2$, add a small volume of $FeCl_3$ solution. Dilute, and boil the solution.
4. To a drop of an acetate solution, on a spot plate, add 1 drop of 5% lanthanum nitrate solution, a drop of an $0.01N$ iodine solution, and several drops of dilute NH_4OH. [$Ba(NO_3)_2$ solution should be added to remove sulfate and phosphate, if they are present.]

ANALYSIS OF GROUP IV ANIONS

(Only Group IV anions present)

1. Treat a small portion of the solid unknown with some concentrated H_2SO_4. Smell the vapors cautiously. If any of the members of this group are present alone, their presence may be indicated by this test.

2. Nitrate.—Dissolve some of the solid unknown in water. Make the solution alkaline with dilute NaOH solution, and boil to expel any NH_3 that may be present. Cool the solution, add some aluminum dust, and boil. Place a piece of moist red litmus paper over the mouth of the tube.

Odor of NH_3, with red litmus turning blue, proves **nitrates.**

3. Chlorate.—Filter off the aluminum dust from the solution from step 2, divide the filtrate into two parts, and reserve one for step 4. Acidify the other portion with dilute HNO_3, and add a slight excess of $AgNO_3$ solution.

White precipitate of AgCl proves **chlorate.**

4. Acetate.—Acidify the second portion of the filtrate from step 2 with concentrated H_2SO_4, add a small volume of ethyl alcohol, and heat.

Pleasant fruity odor of ethyl acetate proves **acetate.**

COMBINED ANALYSIS OF THE ANIONS

1. Test for Group I (the volatile acids) with dilute HCl. If present, proceed as in Group I scheme.

2. Test a sample of the unknown, from which Group I has been eliminated with HCl, for Group II with $BaCl_2$-$CaCl_2$ reagent. If a precipitate is obtained, proceed as in the group procedure.

3. Acidify a fresh sample of the unknown with dilute HNO_3, and add $AgNO_3$ solution. If Group III is present, proceed as previously directed.

4. Treat another fresh portion with solid Ag_2SO_4 or Ag_2CO_3 to remove most of the interferences (*i.e.*, Groups I, II, and III). Filter, and test the filtrate for Group IV.

CHAPTER XVI

COMPLETE ANALYSIS

The analysis of a complete unknown not only requires the application of all the ability and knowledge gained in the previous sections but also introduces some additional difficulties. The sample to be analyzed, usually a solid, can be a mixture of salts, a mineral, an ore, an alloy, or some definite commercial product, such as a paint pigment or a cleaning powder. After applying cation as well as anion analysis, the analyst should present a report that gives a qualitative but accurate account of the entire inorganic composition of the material. The analyst should also give an estimate of the amount of each substance present; *i.e.*, he should be able to state whether the constituents are present in large, medium, or small amounts. For instance, an analysis of Duralumin should read:

Large amount of aluminum.

Medium amount of copper.

Small amounts of magnesium and iron.

Let us now consider briefly the additional difficulties that we may encounter in the course of a complete analysis.

Solution.—The first problem is to dissolve the substance. This often demands a great deal of patience and ingenuity. Certain steels are only so slowly soluble in acids that the student is likely to become discouraged. He should remember that success in the laboratory often requires the patience of a Thomas Edison. Certain types of substances can be dissolved only by special methods. These methods are discussed in the latter part of this section.

Incompatibilities.—Another complication is caused by the interaction of some components of the mixture whenever the substance is dissolved or acidified. Let us assume that we wish to analyze an "effervescent powder" like Citro-carbonate. Upon dissolving this substance in water, a gas would be evolved. By means of the preliminary tests, we should find that the gas was carbon dioxide. We could therefore make the following deductions: (1) The original material must have contained a carbonate or bicarbonate. (2) Some substance must have been present originally that, upon the addition of water, gave an acidic solution. We should now analyze the solution

and find that it contained sodium citrate. Hence we may say that the original substance was a mixture of citric acid and sodium carbonate or bicarbonate. Here we have chosen a very simple example, but in certain instances it is very difficult to decide what the original components were.

Interferences.—The presence of certain substances seriously interferes with the usual course of an analysis. For instance, tartrates and many other organic substances form very stable complexes with iron, aluminum, and chromium. These complexes furnish only minute amounts of the free cations and hence these ions cannot be precipitated by the usual methods. Consequently, before making a Group III cation analysis, the organic substance should be destroyed. Phosphates and oxalates also interfere with the analysis of cation Groups III and IV by forming precipitates of alkaline earth phosphates or oxalates when the solution is made alkaline. These interferences must therefore be removed before analyzing for Group III.

Suggested Order of Analysis.—The order in which the various steps of an analysis are made depends to a certain extent upon the substance. However, the scheme outlined has proved useful generally.

1. *Preliminary Tests.*—The unknown should be subjected to the series of tests that are outlined in the section on blowpipe analysis. These tests very often will rapidly show the analyst how he may materially shorten the course of an analysis. They also invariably give valuable indications as to the principal constituents in the unknown. At this point, the analyst should make a thorough test for the presence of cyanides and carbonates, since it is obviously impossible to detect them in the prepared solution.

2. *Prepared Solution.*—The unknown should be boiled with sodium carbonate solution. (See details in later section.) This operation yields a solution of the sodium salts of the anions and precipitates the interfering cations.

3. *Analysis of the Anions.*—The prepared solution should be analyzed for the anions.

4. *Preparation of a Solution Suitable for Cation Analysis.*—See details in later section.

5. *Cation Analysis.*—If the preliminary tests and the anion analyses indicate the presence of interferences, they should be removed before the analysis of Group III is undertaken.

Prepared Solution.—The unknown is boiled with concentrated Na_2CO_3 solution. The metals are precipitated as the insoluble carbonates and hydroxides, and the filtrate contains the anions plus excess carbonate.

Preparation of a Solution Suitable for Cation Analysis.—All inorganic substances can be classified in either of two groups.

A. Water and Acid-soluble Substances.—The finely ground material is treated with separate portions of cold and hot water, dilute and concentrated hydrochloric acid, dilute and concentrated nitric acid. The order is determined by the following considerations.

ADVANTAGES OF CONCENTRATED HCl AS A SOLVENT.

1. HCl is a nonoxidizing acid.
2. Metallic oxides dissolve more readily in HCl than in HNO_3.
3. Oxidizing substances, when heated with HCl, evolve chlorine and hence indicate their presence.

DISADVANTAGES OF HCl AS A SOLVENT.

1. Arsenous compounds are converted to volatile $AsCl_3$ and hence may be lost.
2. Silver and mercurous mercury are precipitated as insoluble chlorides.

ADVANTAGES OF HNO_3 AS A SOLVENT.

1. Excellent solvent for metals, alloys, and metallic sulfides.

DISADVANTAGES OF HNO_3 AS A SOLVENT.

1. Yields insoluble precipitates of metastannic acid and hydrated antimony oxides with compounds containing tin and antimony.
2. Hot concentrated HNO_3 oxidizes sulfides and sulfites to sulfates and thus causes partial precipitation of the alkaline earth sulfates.

Solution of Alloys.—Small portions of the alloy should be treated with various solvents to determine which is most effective. The best solvents for the usual types of alloys are listed below.

Copper alloys (brass, bronze)....	HNO_3
Steels..........................	HCl
Aluminum alloys...............	HCl
Silver alloys....................	HNO_3
Gold, platinum, and noble metals	Aqua regia
White metals..................	Boiling HCl, to which HNO_3 is added, several drops at a time. This prevents the precipitation of metastannic acid
Tin alloys.....................	Do not use HNO_3 except as given above
High silicon ferrous alloys......	Hot 1:9 HCl and subsequent concentration

The only anions likely to be found in solutions of alloys are phosphate, silicate, and sulfate, which are present originally as phosphides, silicides, and sulfides. Nitric acid is generally the preferred solvent, since it oxidizes these elements to the higher valence states.

B. Substances Insoluble in Water and Acids.—If after all attempts to dissolve the substance in acid have been made, an insoluble residue is left, the number of possibilities is quite limited. The application of the methods of blowpipe analysis will usually furnish us with a tentative identification. For conclusive proof, the special methods of solution, outlined below, should be applied and followed by identification tests.

Alkaline Earth Sulfates.—Fuse with a large excess of an anhydrous Na_2CO_3-K_2CO_3 mixture (1:1). After the mass becomes liquid, heating should be continued for 15 min. Allow to cool, and extract with dilute sodium carbonate solution until the sulfate ion is completely removed. The remaining alkaline earth carbonates are dissolved in HCl.

Lead Sulfate.—Boil extensively with a concentrated sodium carbonate solution, and wash the basic lead carbonate precipitate until the sulfate ion is completely removed. The residue is then dissolved in HNO_3.

Metastannic Acid and Tin Dioxide.—Fuse with a large excess of a sulfur and anhydrous sodium carbonate mixture (1:1). (Keep the crucible covered.) The residue is extracted with warm water. The solution contains tin and other members of Groups II*B*, IV, and V. The residue is dissolved in HNO_3 and tested for small amounts of members of Groups II*A* and III.

Silicic Acid and Silicates.—Fuse with mixture of potassium and sodium carbonate.

Insoluble Fluorides.—Heating with concentrated sulfuric acid yields the corresponding alkaline earth sulfates.

Silver Halides.—Boiling with dilute sulfuric acid and granular zinc yields a black precipitate of metallic silver and a solution containing the corresponding halide ion.

Insoluble Chromium Compounds and Chromites.—Fuse with Na_2CO_3 and $NaNO_3$. A yellow melt that dissolves in water yielding a yellow solution indicates the presence of chromate ion.

Insoluble Complex Cyanides.—Boil with strong NaOH solution, and dilute with water. The anions can be detected in the aqueous solution.

Interferences in Cation Analysis

Phosphate, oxalate, tartrate, and organic matter interfere with the analysis of cation Groups III and IV, either by forming precipitates when the solution is rendered alkaline (phosphate and oxalate) or by preventing the precipitation of certain ions by forming complex ions

(tartrate, citrate, etc.). These interferences must be tested for and removed, therefore, before analyzing for Group III. This necessitates modifying the scheme somewhat.

Removal of Tartrate, Oxalate, and Organic Matter.—Evaporate the filtrate from Group II just to dryness, add concentrated H_2SO_4, and heat until the mass has charred completely. Cool, add a small volume of concentrated HNO_3, and heat until fumes of SO_3 are evolved. Cool and repeat the treatment with HNO_3 until the solution becomes colorless or light straw color. (Usually three to five treatments are sufficient.) Dilute the solution, filter, and analyze the filtrate for Groups III and IV by the usual methods. The residue contains the sulfates of Ca, Ba, Sr, and Cr. Boil the residue for a short time with a solution of Na_2CO_3. Filter and wash the precipitate until the washings are free from sulfate ion. Discard the filtrate and washings. Treat the precipitate with dilute HCl, boil, and filter. Test the filtrate for Ca, Ba, Sr, and Cr. The sodium carbonate treatment transposes the insoluble sulfates to the insoluble carbonates. This transposition is not complete, particularly in the case of $BaSO_4$, but yields sufficient ions so that tests may be performed.

Removal of Phosphate.—Boil the filtrate from Group II until it is free of H_2S. Add a drop of HNO_3, and boil to oxidize all the iron. Test a small sample of the solution for iron with $K_4Fe(CN)_6$. To the remainder of the solution, add ammonium hydroxide cautiously until a slight precipitate, which persists, is obtained, and then just redissolve in dilute HCl. Treat the solution with a quantity of solid $NH_4C_2H_3O_2$ and some $HC_2H_3O_2$. If the solution is not red at this point, add $FeCl_3$ solution until it assumes a deep red color. (Do not use an excess.)

NOTE: The filtrate at this point should give a red precipitate with dilute NH_4OH. A light-colored precipitate indicates that insufficient $FeCl_3$ has been added.

Dilute the solution with ten times its volume of hot water, and boil for several minutes. Filter while hot. The precipitate contains the phosphates and basic acetates of Fe, Al, and Cr and possibly some Ni, Mn, and Zn. The colorless filtrate is concentrated to a small volume, and if a slight precipitate forms, it is filtered off and discarded. The filtrate is then subjected to analysis for the remainder of the cations. The precipitate is treated with solid Na_2O_2 and boiled. The filtrate contains AlO_2^- and $CrO_4^{=}$, which are tested for in the usual manner.

APPENDIX

UNKNOWNS

The analysis of unknowns is the central theme in a course in qualitative analysis. Hence it behooves us to give some attention to the mechanics involved in preparing and dispensing them.

At the Polytechnic Institute, the following system has been used for a number of years and has been found to be very convenient and economical. Of course, many other systems can be and are used. To a large extent, the system that is chosen will depend upon the conditions existing in a particular institution. However, we are describing this system in the hope that it may be of some value.

Master Solutions of the Cations.—A master solution is prepared of the nitrate of each of the cations analyzed for in the scheme (except those of Group II*B*, for which solutions of the chlorides are also prepared, and chromium, whose sulfate often may be used). This master solution has a concentration equal to ten times the concentration of the test solutions (as given in the section on solutions). Usually, 1 or 2 liters of each of these solutions is prepared. (From these master solutions, the test solutions may be readily prepared by dilution.) These solutions are stabilized by adding the corresponding acids. They are kept in glass-stoppered bottles from year to year.

Stock Solutions of Unknowns.—From these master solutions, stock solutions of the unknowns are prepared. For instance, if we wished to prepare a stock solution containing Ag, Cu, As, Ni, Co, Ca, and Na, we should add 100 ml. of the master solution of each cation to a liter bottle and fill the bottle with distilled water, acid, or both. These stock solutions are serially numbered from one up (at least two labels to each bottle), and the key to the cations in each bottle is kept in the possession of the instructor. There is no way of discovering from the number on a bottle what any unknown contains, unless one possesses the unknown book. These stock solutions are usually stable and are kept from year to year. Some are prepared annually, some biannually, some triannually, etc., as the solution becomes exhausted.

Dispensing Unknowns.—During the summer or shortly before the fall semester begins, a number of kits of unknowns is prepared, sufficient for the following year. Each student, upon registering in the laboratory, receives a kit containing the minimum number of unknowns which he must complete, and his name is entered on the appropriate page in the book. (Extra unknowns are dispensed individually as needed.) Each kit bears on the box a serial number that refers to a page in the record book of the instructor. The unknowns themselves are numbered 1, 2, 3, etc. These numbers indicate the order in which the unknowns are to be performed. The student is told that unknown 1 contains Group I; number 2, Group II*A*; number 3, Group II*B*; number 4, Groups I and II, etc. The student at no time knows the serial number of a particular unknown. Hence shopping around by the student in order to find someone who has the same number is eliminated. If the system described below is used in filling the kits, the probability that two kits will contain the same unknowns is extremely slight.

The Kits.—The kits themselves are small cardboard boxes that can be made to order by any manufacturer of cardboard boxes. They are not returnable and are usually discarded by the student at the end of the year. The liquid unknowns are dispensed in 8-dram (short style, patent lip) vials and stoppered with corks. Each vial holds about 30 ml., but the vials are not completely filled. Hence each student gets about 20 to 25 ml. of unknown, which is sufficient for from five to eight analyses. Thus the need for refills is largely eliminated. Our practice at the Polytechnic Institute has been to stamp the number of the unknowns with a rubber stamp on the cork of each bottle. We find this method much faster than pasting labels on the bottles. The number of mix-ups due to the interchanging of corks is, we find, negligible.

Filling the Kits.—The method described below for filling the kits is, we believe, almost foolproof; *i.e.*, in the last five years that we have been using it, there has been but one case where a student received an unknown whose serial number was not correctly inscribed in the record book. The method has thus practically eliminated the common complaint, "I got the wrong unknown."

The method used can be outlined thus:

1. A record book is obtained with numbered pages.
2. The kit boxes are numbered to correspond to the pages of the book; *i.e.*, if the kit were numbered 42-34, the unknowns contained therein would have their serial numbers inscribed on page 34 of the 1942 record book.
3. The kits are then arranged in order of their numbers.
4. All the liter bottles containing the solutions of the Group I unknowns are then placed on a laboratory bench.
5. The required number of vials (equal to the number of kits) is counted out, and they are distributed among the liter bottles; *i.e.*, if there are 5 Group I unknowns and 50 kits, 50 vials are counted out and 10 placed in front of each bottle.
6. The vials in front of each bottle are filled from that bottle and replaced in front of that bottle.
7. The vials are stoppered.
8. Every cork is stamped with the number 1.
9. The vials in front of the first bottle are then distributed among the kits. As each vial is placed in a kit box by an assistant, the serial number of the unknown is recorded on the appropriate page of the record book—the number of the page is the same as the number of the kit—by another person. (This operation is accomplished most expeditiously by two persons.)
10. When the vials in front of bottle 1 are distributed, the bottle containing that unknown is set aside, and the vials in front of bottle 2 are distributed—and so on, until all the vials containing the first unknown have been distributed. At this point, every kit should have one vial, and there should be no extra vials.
11. After this check, the same procedure is repeated for the second unknown—and so on, until all the kits have been filled.

Solid Unknowns.—The anion and blowpipe unknowns are dispensed in the form of solid salts in 2-dram vials (about three-fourths full). The same system is followed in distributing these unknowns.

Preparation of Solid Unknowns.—Prepared solid unknowns are kept in screw-cap bottles, each of which has a serial number. About ½ to 1 lb. of each unknown is prepared at one time. (This will vary with the number of unknowns, number of unknowns in a given series, etc.) The various salts (ground, if necessary, in a corn

mill) are sieved through a 20-mesh sieve. This must be done even for very fine powders, since many fine powders form lumps. The required amounts of each powder are then violently shaken together in a large bottle until they are thoroughly mixed. They are then transferred to the stock bottle.

Conclusions.—This method, although it seems involved and appears to be quite time-consuming, is, in practice, quite simple and routine. As an example, an assistant working 4 hr. a day and a student working 7 hr. a day for 10 days filled, labeled, and recorded 1,440 vials of liquids and 600 vials of solids. In addition, they prepared master solutions and unknown stock solutions as needed.

During the course of the year, very little extra time is needed. Additional unknowns performed for extra credit must be filled, and very occasionally, refills are needed. These refills are very easily made, since all the instructor needs to do is to consult the record book to see what the serial number of the unknown is and then to fill the student's vial from the appropriate stock bottle.

MINIMUM LIST OF EQUIPMENT FOR EACH STUDENT FOR CATION ANALYSIS

12 test tubes, 10 by 75 mm. Pyrex
2 test tubes, 13 by 100 mm. Pyrex
1 test tube, 20 by 150 mm. Pyrex
1 test tube, side arm 5 in.
1 test-tube rack
1 test-tube holder (spring clothespin)
1 crucible, 15 ml.
1 crucible, 5 ml.
2 beakers, 250 ml.
1 flask, 500 ml. (for wash bottle)
1 graduate, 10 ml.
2 microscope slides, 3 by 1 in.
6 stirring rods, 3 mm. by 8 in.
12 medicine droppers (4-in. glass part)
1 spot plate
1 microburner
1 ring stand and 2 rings
1 burette clamp
1 piece platinum wire, 2 in.
1 sand pan
1 water bath
1 piece rubber tubing, 3⁄16 by 3⁄64, 12 in. long
1 piece rubber tubing, 1⁄4 by 1⁄8, 24 in. long
25 sheets filter paper, Whatman No. 1, 11 cm.
100 strips each litmus paper, red and blue
Glass tubing, 7-mm. soft glass
Rubber and cork stoppers
Absorbent cotton
Aitch-Tu-Ess cartridges
Reagent bottles
Centrifuge (1 for each 10 to 12 students)
Hand spectroscope (1 for each 25 students)

Additional Equipment for Blowpipe and Anion Analysis

1 lead dish
1 glass square, 3 by 3 in., soft glass
1 blast lamp (for class)
1 Bunsen burner
1 hammer
1 anvil
1 blowpipe
1 blowpipe tip
1 charcoal borer (knife point may be used)
Charcoal blocks
Plaster of Paris tablets

SOLUTIONS

* Indicates that the substance is used in the scheme, or more than five times in the Laboratory part.

† Indicates that the substance is used from three to five times in the Laboratory part.

‡ Indicates that the substance is used only once or twice in the Laboratory part.

§ Indicates that the substance is used in the scheme, or more than five times in *only* the Anion and Blowpipe sections.

‖ Indicates that the substance is used less than five times in only the Anion and Blowpipe sections.

Acetic Acid.
concentrated: glacial, approximately $17N$*
dilute; 1 part acid to 2 parts H_2O, approximately $6N$*
solution; 30 per cent; prepare as needed§

Alizarin S Blue.
solution: 0.5 g./liter of 50 % acetone. Add 1 ml. concentrated acetic acid*

Aluminon.
solution: 0.1 % aqueous solution*

Aluminum Dust.
solid§

Aluminum Nitrate.
test solution: 70 g. $Al(NO_3)_3 \cdot 9H_2O$/liter solution; add 8 ml. of concd. HNO_3*

Ammonium Acetate.
solution $3N$: 231 g./liter solution‡
saturated aqueous solution*
solid*

Ammonium Benzoate.
solution: 7 % in water*

Ammonium Carbonate.
solution $6N$: 250 g. powdered commercial ammonium carbonate dissolved in 1 l. of $6N$ NH_4OH (commercial ammonium carbonate is $NH_4HCO_3 \cdot NH_4CO_2NH_2$)†

Ammonium Chloride.
saturated aqueous solution‡
solid*

Ammonium Chromate.
solution $0.5N$: 38 g./liter of solution*

Ammonium Hydroxide.
concentrated about $15N$*
dilute $6N$: (2 parts NH_4OH:3 parts H_2O)*

Ammonium Molybdate.
solution: dissolve 50 g. of 85 % molybdic acid in a mixture of 120 ml. of H_2O and 70 ml. of NH_4OH. Filter, add 30 ml. of HNO_3, and cool. Add the solution, with constant stirring, to a mixture of 200 ml. HNO_3 and 480 ml. of H_2O. Filter or decant solution before use.*

Ammonium Nitrate.
test solution: 44.4 g./liter solution*

Ammonium Oxalate.
solution $0.5N$: 35 g./liter solution*

Ammonium Persulfate.
solid‡

Ammonium Polysulfide.
solution: saturate 200 ml. of ice-cold concd. NH_4OH with H_2S. Add 200 ml. of concd. NH_4OH. Dilute to 1 l., and digest for several hours with 25 g. of flowers of sulfur. Filter.*

Ammonium Sulfate.
solution $0.5N$: 33 g./liter solution*

Ammonium Thiocyanate.
solution: saturated solution in acetone (NOTE: inflammable reagent)*

Amyl Alcohol (iso).
as commercially bought*

Aniline Sulfate.
solution: 3 % aqueous solution‖

Antimonous Chloride.
test solution: 19 g./liter of dilute HCl*

Antimonous Oxide.
solid‖

Arsenic Nitrate.
test solution: dissolve 15.3 g. As_2O_5 in a liter of dilute HNO_3*

Arsenous Chloride.
test solution: dissolve 13.2 g. of As_2O_3 in a liter of dilute HCl*

Arsenous Oxide.
solid‖

Arsenous Sulfide.
solid‖

Asbestos Fiber*.

Barium Chloride.
solution $1N$: 122 g. $BaCl_2{\cdot}2H_2O$/liter solution‡
solid§

Barium Chloride-Calcium Chloride Reagent.
solution: 240 g. $BaCl_2{\cdot}2H_2O$ and 219 g. $CaCl_2{\cdot}6H_2O$/liter of solution§

Barium Hydroxide.
saturated aqueous solution§

Barium Nitrate.
test solution: 19.0 g. $Ba(NO_3)_2{\cdot}2H_2O$/liter of solution*

Barium Peroxide.
solid‖

Benzidine (Benzidine Acetate).
solution: 0.5 g. benzidine in 100 ml. concd. acetic acid and dilute to 1 l.*

α-Benzoin Oxime.
solution: 5 % alcoholic solution*

Bettendorf's Reagent.
saturated solution of stannous chloride in concentrated HCl*

Bismuth Chloride.
solid‖

Bismuth Flux.
solid: equal parts of KI and sulfur ground together*

Bismuth Nitrate.
test solution: 23.2 g. of $Bi(NO)_3 \cdot 5H_2O$/liter of dilute HNO_3*

Boric Acid.
solid||

Bromine Water.
saturated aqueous solution (some liquid bromine should be left at the bottom of the bottle)*

Brucine (Alkaloid).
solid||

Cacotheline.
saturated aqueous solution. Preparation of reagent: dissolve 20 g. of dry brucine in 100 ml. of $5N$ HNO_3 in the cold; then warm to 50 to 60° C. for 15 min. Crystals of cacotheline separate out. Cool in ice water, and allow crystallization to become complete. Filter with suction, and wash with N HNO_3, acetone and ether. Yield should be about 22 g. of yellow powdery crystals*

Cadmium Carbonate.
solid||

Cadmium Chloride.
solid||

Cadmium Nitrate.
test solution: 27.5 g. $Cd(NO_3)_2 \cdot 4H_2O$/liter of solution. Use 3 ml. of concd. HNO_3*

Calcium Acetate.
solid||

Calcium Carbonate.
solid||

Calcium Chloride.
solution $0.5N$: use 55 g. $CaCl_2 \cdot 6H_2O$/liter of solution*
solid||

Calcium Fluoride.
solid||

Calcium Nitrate.
test solution: use 58.9 g. $Ca(NO_3)_2 \cdot 4H_2O$/liter of solution*

Carbon Tetrachloride.
liquid as bought§

Carnot's Reagent.
solution: (freshly prepared) 1 drop of $0.5N$ bismuth nitrate solution is mixed with 2 to 3 drops of $0.5N$ sodium thiosulfate solution and 10 to 15 ml. of absolute alcohol added. (Any turbidity is removed by the careful addition of water)‡

Chromic Nitrate.
test solution: use 77 g. of $Cr(NO_3)_3 \cdot 9H_2O$/liter of solution*

Chromic Sulfate.
test solution: use 68.9 g. $Cr_2(SO_4)_3 \cdot 18H_2O$/liter of solution. Add 10 ml. concd. H_2SO_4*

Cinchonine.
solution: dissolve 10 g. cinchonine in a liter of hot water containing some HNO_3, cool, and add 20 g. KI*

Cobaltous Nitrate.
test solution: use 49.4 g. $Co(NO_3)_2 \cdot 6H_2O$/liter of solution. Add 8 ml. of HNO_3*
solution $2N$: 291 g. $Co(NO_3)_2 \cdot 6H_2O$/liter of solution. Add HNO_3§

Copper.
foil‡

Cupric Acetate.
solid‖

Cupric Chloride.
solid‖

Cupric Nitrate.
test solution: 38 g. $Cu(NO_3)_2 \cdot 3H_2O$/liter of solution*

Cupric Sulfate.
solution $0.5N$: 63 g. $CuSO_4 \cdot 5H_2O$/liter of solution‖

Dimethyl Glyoxime.
1 % alcoholic solution*

Diphenylamine Acetate.
solution: 1 g. diphenylamine dissolved in 100 g. glacial acetic acid*

Diphenyl Carbazide.
saturated alcoholic solution*

Ethyl Alcohol.
95 % liquid§

Ethyl Ether.
purified (U.S.P.)*

Ferric Chloride.
solution $3N$: 270 g./liter of solution§

Ferric Nitrate.
test solution: 72.4 g. $Fe(NO_3)_3 \cdot 9H_2O$/liter of solution; use 20 ml. HNO_3*

Ferrous Ammonium Sulfate.
solid§
test solution: prepare as needed from clean crystals‡

Ferrous Sulfate.
use ferrous ammonium sulfate‡

Fluorescein Paper.
paper: dip filter paper in a saturated solution of fluorescein in alcohol-water

Hydrochloric Acid.
concentrated: about $12N$*
dilute: $6N$ (1:1)*
solution $0.2N$: prepare as needed by dilution*

Hydrogen Peroxide.
3 % U.S.P. solution*

Iodine Solution.
solution $0.01N$: 1.3 g. of iodine/liter of solution containing some KI‖

Lanthanum Nitrate.
solution 5 %: 5 g. dissolved in 95 ml. H_2O‖

Lead Acetate.
solution: 95 g. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$/liter of solution‖
paper: moisten piece of filter paper with reagent‡

Lead Nitrate.
test solution: 16 g. $Pb(NO_3)_2$/liter of solution; use 2 ml. HNO_3*

solid||
solution: 165 g./liter of solution§

Magnesia Mixture.
solution: Dissolve 52 g. $MgCl_2 \cdot 6H_2O$ and 134 g. NH_4Cl in water, add 350 ml. of concd. NH_4OH, dilute to 1 l. Use only freshly filtered or decanted liquid*

Magnesium Metal.
ribbon*

Magnesium Nitrate.
test solution: 106 g. $Mg(NO_3)_2 \cdot 6H_2O$/liter of solution*

Manganese Dioxide.
solid||

Manganous Chloride.
solution: saturated solution of $MnCl_2 \cdot 4H_2O$ in concd. HCl (freshly prepared)§
solid§

Manganous Nitrate.
test solution: 53 g. $Mn(NO_3)_2 \cdot 6H_2O$/liter of solution or 69 g. of 75 % solution/liter (75 % solution is sold commercially)*

Manganous Sulfate.
solid ($MnSO_4 \cdot 4H_2O$)||

Mercuric Chloride.
solution 0.4N: 54 g./liter of solution*
solid||

Mercuric Iodide.
solid||

Mercuric Nitrate.
test solution: 16 g. $Hg(NO_3)_2 \cdot \frac{1}{2}H_2O$/liter of solution; use 17 ml. HNO_3*
solution: 10 g. $Hg(NO_3)_2 \cdot \frac{1}{2}H_2O$/100 g. H_2O; use 1 ml. HNO_3||

Mercuric Oxide Yellow.
solid||

Mercurous Nitrate.
test solution: 14 g. $Hg_2(NO_3)_2 \cdot 2H_2O$/liter of solution; use 50 ml. HNO_3*

Methyl Orange.
solution: 0.1 % aqueous solution||

Naphthylamine Acetate.
solution: boil 0.2 g. of solid α-naphthylamine with 20 ml. of H_2O, pour off colorless solution, and add to it 150 ml. of 2N acetic acid§

Nickelous Nitrate.
test solution: 49.5 g. of $Ni(NO_3)_2 \cdot 6H_2O$/liter of solution; use 10 ml. of HNO_3*

Nitric Acid.
concentrated: approx. 15N*
dilute: approx. 6N (2:3)*

p-Nitrobenzene-azo-resorcinol.
solution 0.001 %: 0.001 g. dissolved in 100 ml. of 2N NaOH*

solid*
solution: make fresh as needed; saturated solution in 2 drops of 50 % acetic acid*

Oxalic Acid.
solid||

Paraffin.
solid||

Perchloric Acid.
60 % solution‡
Phenolphthalein.
1 % alcoholic solution||
Picric Acid.
saturated aqueous solution‡
Potassium Acetate.
solid§
Potassium Bromide.
solid||
Potassium Chlorate.
solid*
Potassium Chloride.
solid‡
Potassium Chromate.
solution: 5 % aqueous solution*
solid||
Potassium Cyanide.
solution: 3 %*
solid||
Potassium Dichromate.
solid||
Potassium Ferricyanide.
solution: 5 % aqueous*
solid||
Potassium Ferrocyanide.
solution: always freshly prepared from clean crystals*
solid*
Potassium Hydroxide.
solid||
Potassium Iodide.
solid||
solution $1N$: 166 g./liter of solution*
solution $0.1N$: prepare by dilution as needed‡
Potassium Nitrate.
test solution: 26 g./liter of solution*
solid||
Potassium Nitrite.
solid*
Potassium Permanganate.
solution $0.1N$: 3.2 g./liter of solution*
Potassium Thiocyanate.
solution: 97 g./liter of solution*
Pyridine.
liquid‡
Rhodamine B.
solution: 0.1 g. of tetraethylrhodamine/liter of solution*
Rhodanine Solution.
solution: 0.3 g. of *p*-dimethylamino benzalrhodanine in 1 l. of acetone*
Sand.
pure quartz sand, "Ottawa sand"||

Silver Carbonate.
solid‖
Silver Nitrate.
test solution: 15.8 g./liter of solution*
solution 0.1*N*: use test solution*
solution 50%: 50 g. $AgNO_3$/50 ml. of H_2O‡
solution 0.05%: prepare by diluting 50% solution*
solid‡
Silver Sulfate.
solid‖
Sodium Acetate.
solid*
saturated solution*
Sodium Ammonium Hydrogen Phosphate (Microcosmic Salt).
solid‖
Sodium Arsenate.
test solution: 22.5 g. of $Na_2HAsO_4 \cdot 7H_2O$/liter of solution*
solid§
Sodium Arsenite.
solid§
Sodium Azide-Iodine Reagent.
solution: in 100 ml. of 0.1*N* I_2 solution, dissolve 3 g. of sodium azide‖
Sodium Bicarbonate.
solution 0.01*N*: 0.84 g./liter of solution‖
solid§
Sodium Bismuthate.
solid*
Sodium Carbonate.
solution 3*N*: 159 g./liter of solution*
solution 0.01*N*: 0.5 g./liter of solution‖
solid anhydrous‖
Sodium Chloride.
solution 5%: 50 g. in 950 ml. of H_2O§
solid‖
Sodium Cobaltinitrite.
solution: prepare fresh as needed*
solid*
Sodium Fluoride.
solid‖
Sodium Hydroxide.
solution 6*N*: 240 g./liter of solution*
Sodium Hypobromite.
solution: prepare fresh as needed: to a solution of bromine water add NaOH until the solution is yellow; then add as much NaOH as was previously added*
Sodium Nitrate.
test solution: 37 g./liter of solution*
solid‖
Sodium Nitrite.
solid*
Sodium Nitroprusside.
solution: 1 g./100 ml. of H_2O§

Sodium Oxalate.
solid||
Sodium Peroxide.
solid*
prim. Sodium Phosphate NaH_2PO_4.
solid||
sec. Sodium Phosphate.
solid||
solution 10%: 100 g. of $Na_2HPO_4 \cdot 12H_2O$/900 g. of H_2O§
tert. Sodium Phosphate.
solid||
Sodium Potassium Tartrate.
solid||
Sodium Stannite.
solution: must be freshly prepared by the student; to a stannous chloride solution add NaOH until the precipitate that forms redissolves (the solution should be alkaline)*
Sodium sulfate.
solid||
Sodium Sulfide.
solid||
Sodium Sulfite.
solid§
Sodium Tetraborate (Borax).
solid§
Sodium Thiosulfate.
solution 0.5N: 62 g./liter of solution*
solid§
Stannic Chloride.
test solution: 29.5 g. $SnCl_4 \cdot 5H_2O$ dissolved in 400 ml. of 6N HCl dilute to 1 l.*
Stannous Chloride.
test solution: 19.0 g. $SnCl_2 \cdot 2H_2O$ dissolved in 1 l. of solution; use 100 ml. concd HCl*
solution 0.5N: 56 g. dissolved in 1 l. of solution containing some HCl; add a piece of metallic tin*
Starch-iodide Paper.
paper can be purchased*
Strontium Chloride.
solution 1N: 133 g. $SrCl_2 \cdot 6H_2O$/liter of solution§
solid||
Strontium Nitrate.
test solution: 24.2 g. of $Sr(NO_3)_2$/liter of solution*
Sulfanilic Acid.
solution: 0.5 g. in 150 ml. of 2N acetic acid||
Sulfuric Acid.
concentrated: about 36N*
dilute: 6N (1:5)*
Tartaric Acid.
solid||
Thiosinamine (Allyl Thiourea)
solid*

Tin.
solid granulated*

Turmeric Paper.
paper as bought||

Zinc Metal.
granular||
stick (As free)*

Zinc Chloride.
solid||

Zinc Nitrate.
test solution: 45.5 g. $Zn(NO_3)_2 \cdot 6H_2O$/liter of solution*

Zinc Nitroprusside.
paste: prepare as needed; add concentrated zinc sulfate solution to a sodium nitroprusside solution; filter off the precipitate, and use as a paste§

Zinc Oxide.
solid||

Zinc Sulfate.
solution: 25 g./100 ml. H_2O§

Zinc Uranyl Acetate.
solution: dissolve 100 g. of uranyl acetate in 60 g. of 30% acetic acid, warming, if necessary; dilute to 500 ml. (solution *A*); dissolve 300 g. of zinc acetate in 30 g. of 30% acetic acid, and dilute to 500 ml. (solution *B*). Mix *A* and *B*; add a trace of NaCl; allow to stand 24 hr.; filter*

LOGARITHMS OF NUMBERS[1]

Natural numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts. 1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

[1] *From Millard, E. B., "Physical Chemistry for Colleges."*

LOGARITHMS OF NUMBERS

Natural numbers.	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS.								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	7376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

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